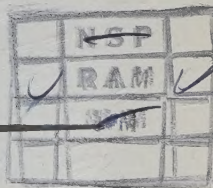


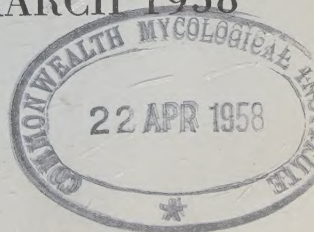
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NEW ZEALAND JOURNAL OF SCIENCE



VOL. 1 NO. 1

MARCH 1958



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General

Papers published, or offered for publication, elsewhere are not acceptable. Nevertheless, publication elsewhere of an abstract or of an extended summary does not preclude publication in full in this journal.

Typescript

The original and one carbon copy are required, on one side only of foolscap paper, double spaced, with a left-hand margin of at least one inch and a quarter. Reasonably heavy good-quality paper should be used. flimsy paper delays the machine operator and consequently increases the cost of printing.

A brief summary is required, at the beginning of the paper. It should indicate the scope of the paper and give the principal results, and should be suitable for reproduction by abstracting journals as it stands.

All matter to be printed in italic type (e.g., generic and specific names) must be underlined.

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Titles should be as brief as possible.

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These are to be numbered consecutively in arabic numerals, regardless of whether they are half-tones (photographs) or line blocks (graphs, etc.). Each must be referred to in the text, and only such figures as are essential to elucidate the text can be published.

The author's name, the title of the paper (abbreviated), and the figure number should be written lightly in soft pencil on the back of each figure.

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If the scale is important, it should be shown on the figure, or, alternatively, the magnification or reduction may be stated in the caption, taking into account the printing reduction.

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In the text, citations are to be by author's name and year, e.g. "Brown, 1957)" or "... as stated by Brown (1957)". The list of references at the end of the paper is to be arranged in alphabetical order of authors' names. Titles of papers cited may be included or omitted; if included, all words other than conjunctions, pronouns, and prepositions are to have capital letters. Titles of periodicals are to be abbreviated in accordance with the "World List of Scientific Periodicals", 3rd ed. 1952. The title of the periodical and the volume (and part) number are to be underlined for italics, but not the page number(s). Titles of books are to be inverted commas and not underlined; the name and location of the publisher are to be given. For arrangement, punctuation, etc., of references, see examples in this issue.

NEW ZEALAND JOURNAL OF SCIENCE

Department of Scientific and Industrial Research, Wellington

Editor: Mabel Rice

VOL. 1

MARCH 1958

NUMBER 1

THE ESTIMATION OF MISSING VALUES IN FACTORIAL EXPERIMENTS

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(Received for publication, 20 March 1957)

Summary

A formula for estimating a missing value in any complete factorial experiment by minimizing the highest-order interaction is derived and illustrated. The missing value may be interpreted as the value required to make a certain component of this interaction equal to zero. These results have been published elsewhere, without proof. When there are more than four factors, the general formula is unnecessarily complex; simpler formulae are presented.

INTRODUCTION

A discussion of methods of estimating missing values was given by Goulden (1952). Cochran and Cox (1950) gave some applications to factorial experiments, but did not present a general formula; their recommendation for a single complete replication, to minimize the sum of squares for the interactions that are used as error, is, of course, all that is needed, if these interactions are decided on before fitting the missing value.

GENERAL FORMULA

If an experiment consists of one complete replication of an $a \times b \times c \dots \times f$ factorial, with n factors $A, B, C, \dots, F$ at $a, b, c, \dots, f$ different levels respectively, then a suitable estimate, y , of a missing value may be obtained by minimizing the highest-order inter-

action sum of squares. The sum of squares is expressed as a function of y , and differentiated with respect to y . To obtain this sum of squares the other sums of squares, for main effects and interactions, may be written retaining only terms in y , in anticipation of the differentiation. Then, if $abc \dots f = p$, and if (G) is the sum of the available observations—i.e., the incomplete grand total; (A) is the sum of the $bc \dots f - 1$ observations for the level of A which contains the missing value—i.e., the incomplete A total; (AB) is the incomplete $A \times B$ total, and so on up to $(BC \dots F)$, which is the sum of $a - 1$ observations, the total sum of squares is

$$TSS = y^2 - \frac{2(G)y + y^2}{p}.$$

$$\text{Further, } pSS(A) = a\{2(A)y + y^2\} - \{2(G)y + y^2\}$$

$$= y^2(a - 1) + 2y\{a(A) - (G)\},$$

$$pSS(B) = y^2(b - 1) + 2y\{b(B) - (G)\},$$

$$pSS(C) = y^2(c - 1) + 2y\{c(C) - (G)\},$$

$$pSS(A \times B) = ab\{2(AB)y + y^2\} - a\{2(A)y + y^2\} \\ - b\{2(B)y + y^2\} + \{2(G)y + y^2\}$$

$$= y^2(a - 1)(b - 1) + 2y\{ab(AB) \\ - a(A) - b(B) + (G)\},$$

$$pSS(A \times C) = y^2(a - 1)(c - 1) + 2y\{ac(AC) \\ - a(A) - c(C) + (G)\},$$

$$pSS(B \times C) = y^2(b - 1)(c - 1) + 2y\{bc(BC) \\ - b(B) - c(C) + (G)\},$$

$$pSS(A \times B \times C) = abc\{2(ABC)y + y^2\} - ab\{2(AB)y + y^2\} - \dots \\ + a\{2(A)y + y^2\} + \dots - \{2(G)y + y^2\}$$

$$= y^2(a - 1)(b - 1)(c - 1) + 2y\{abc(ABC) \\ - ab(AB) - ac(AC) - bc(BC) + a(A) \\ + b(B) + c(C) - (G)\},$$

and so on. The author is indebted to a referee for a simplification used in the above derivation.

If there are only three factors, $(ABC) = 0$, and

$$\frac{d}{dy} \{SS(A \times B \times C)\} = 0 \text{ when}$$

$$(a-1)(b-1)(c-1)y = G - a(A) - b(B) - c(C) \\ + ab(AB) + ac(AC) + bc(BC).$$

Expressions for the higher-order interaction sums of squares may be derived in turn, and it is found that the highest-order interaction sum of squares is given by

$$pSS(A \times B \times C \dots \times F) = y^2 \{p - p/a - p/b - \dots \\ + p/ab + \dots + (-1)^n\} \\ + 2y\{p \cdot 0 - p(BC \dots F)/a - p(AC \dots F)/b - \dots \\ + p(C \dots F)/ab + \dots + (-1)^n(G)\},$$

and by differentiating and rearranging, the general formula for y is

$$(-1)^{n-1}(a-1)(b-1)(c-1) \dots (f-1)y \\ = (G) - a(A) - b(B) - c(C) - \dots \\ + ab(AB) + ac(AC) + \dots - abc(ABC) \\ - \dots + (-1)^{n-1} bc \dots f(BC \dots F),$$

(Wright, 1956). The right-hand side has $2^n - 1$ terms. For two factors this reduces to the well-known randomized block formula

$$(a-1)(b-1)y = a(A) + b(B) - (G).$$

APPLICATIONS

(1) In a 2^n factorial, the highest-order interaction sum of squares has one degree of freedom and is the square of a linear function of the observations with unit coefficients. A missing value, to make this interaction zero, is easy to calculate directly, though the general formula holds. Goulden (1952) gave the direct method for a 2×2 factorial.

In a three-factor manurial trial analysed recently, the combination of all three nutrients had not been used. The data were analysed using missing values calculated for each of the replications separately: the analysis was adequate to show that no treatment responses approached significance.

To illustrate, the results in the first replicate were

<i>O</i>	<i>A</i>	<i>B</i>	<i>AB</i>	<i>C</i>	<i>AC</i>	<i>BC</i>	<i>ABC</i>
28.9	28.8	25.4	27.3	28.7	24.4	26.5	<i>y</i>

The direct estimate of *y* is given (*cf.* Yates, 1937, Table 4) by

$$28.9 - 28.8 - 25.4 + 27.3 - 28.7 + 24.4 + 26.5 - y = 0,$$

$$y = 24.2.$$

To apply the general formula, the incomplete totals are

(<i>G</i>)	(<i>A</i>)	(<i>B</i>)	(<i>C</i>)	(<i>AB</i>)	(<i>AC</i>)	(<i>BC</i>)
190.0	80.5	79.2	79.6	27.3	24.4	26.5

$$\text{and } y = 190.0 - 2(80.5 + 79.2 + 79.6) + 4(27.3 + 26.5 + 24.4)$$

$$= 24.2.$$

(2) Gutstein (1954) presented results of determinations of total and free β -amylase made on three varieties of barley grown in four localities in one season and in three of the localities the following season. A discussion of the results, and of information not extracted from them by Gutstein, has been given by Stern and Wright (1956). The data for free amylase in three localities are presented (rounded off from Gutstein's figures) in Table 1.

TABLE 1.—Free β -Amylase of Three Barley Varieties in Two Seasons and Three Localities (Gutstein, 1954).

	V1		V2		V3	
	S1	S2	S1	S2	S1	S2
L1	288	267	154	154	108	120
L2	250	263	131	143	135	46
L3	218	356	95	221	85	130

The value for the third variety in the second season and second locality was remarkably low, and although the results, particularly for the third locality, were not consistent it was thought, from experience of similar biochemical analyses, that the sample must have been very

poor in quality, or that a mistake had been made. The total amylase content of the sample was reasonably high, and when the data were expressed as percentages of the total amylase the discrepancy was clearer. It appeared that seasonal, variety, and locality differences might have acted multiplicatively rather than additively to give this value, and that the results would be more consistent if a missing value were substituted. Tukey (1949) developed a test for non-additivity which makes clear whether any particular observation is contributing excessively to interaction, but in the present example, a comparison of the observed figure with that obtained from the rest of the data as a missing value is more simple, though subjective.

The three estimates obtained by applying the standard randomized-block formula to the data from the three localities after totalling over variety, season, and locality in turn were 260, 42, and 212 respectively. As the final analysis of the data from the four localities had a standard error of only 26 units, it is obvious that none of these estimates can be taken seriously—they show only that first-order interactions were large. The general formula was applied, becoming

$$4y = (G) - 3(V) - 2(S) - 3(L) + 6(VS) + 9(VL) + 6(SL),$$

from which $y = 115$.

Substitution of this result made little difference in the analysis and interpretation of the free amylase data, and would have no justification statistically. However, its use with the observed total amylase values to calculate percentage of free amylase was valuable: the seasonal differences in percentage free amylase became non-significant, as found in New Zealand (Stern and Wright, 1956), and the $V \times L \times S$ interaction sum of squares was reduced from 185 (4d.f.) to 103 (3d.f.). Accordingly, it is felt that the use of the calculated value in place of the observed one was justified.

SIMPLER FORMULAE

To estimate error in complex factorial experiments, the higher-order interactions are grouped, and a missing value may be derived from the total error sum of squares, as recommended by Cochran and Cox (1950). The following results may be verified from the relations given above.

- (i) If the total sum of squares is minimized,

$$(p - 1)y = (G);$$

y is estimated (inadequately) as the average of the observations.

- (ii) Using all interactions in the error sum of squares,

$$(p - \Sigma a + n - 1)y = \Sigma a(A) - (n - 1)(G).$$

For the data of the first application above,

$$4y = 2(A) + 2(B) + 2(C) - 2(G),$$

but this estimate (24.6) is not reliable, as it is not influenced by the values of three of the observations, in this case those for the factors applied singly.

(iii) Using all except two-factor interactions for error,

$$\begin{aligned} &\{p - \Sigma ab + (n-2)\Sigma a - \frac{1}{2}(n-1)(n-2)\}y \\ &= \Sigma ab(AB) - (n-2)\Sigma a(A) + \frac{1}{2}(n-1)(n-2)(G). \end{aligned}$$

For $n=3$, this is identical with the general formula.

(iv) Using all except two- and three-factor interactions for error,

$$\begin{aligned} &\{p - \Sigma abc + (n-3)\Sigma ab - \frac{1}{2}(n-2)(n-3)\Sigma a \\ &\quad + \frac{1}{6}(n-1)(n-2)(n-3)\}y \\ &= \Sigma abc(ABC) - (n-3)\Sigma ab(AB) + \frac{1}{2}(n-2)(n-3)\Sigma a(A) \\ &\quad - \frac{1}{6}(n-1)(n-2)(n-3)(G). \end{aligned}$$

One or other of the last two equations should be suitable for use in any experiment with more than three factors. They are similar to the general formula in structure, but have fewer terms, and binomial coefficients. For the last equation, $\frac{1}{6}(n^3 + 5n + 6)$ incomplete totals are required, less than the number $(2^n - 1)$ in the general formula when there are more than four factors.

It has not been realized in the past that the one degree of freedom "lost" in using the general formula has a specific meaning. If the formula is expanded in terms of individual observations and simplified, it may be verified that what is in effect being done is equating to zero the component of the highest-order interaction which measures the interaction of the comparisons of the level of each factor in which the missing value occurs with all other levels of the factor. This leads to an alternative method of obtaining the result given by the general formula.

For example, in the data of Gutstein (1954), the interaction of the seasonal difference with (the comparison of the third variety with the other two) with (the comparison of the second locality with the other two) is made identically zero.

Accordingly, the meaning, in terms of the experimental data, of the fitted missing value could be brought out by deriving it from the expansion of

$$\{(a-1)A_m - \sum_{i \neq m} A_i\} \{(b-1)B_n - \sum_{j \neq n} B_j\} \dots \dots$$

$$\{(f-1)F_t - \sum_{k \neq t} F_k\} = 0,$$

in which the summations run from 1 to $a, b, \dots f$ respectively, the product $A_x B_y C_z \dots F_w$ represents the observation at levels $x, y, z, \dots w$ of the factors, and the missing observation is $A_m B_n C_o \dots F_t$ (Wright, 1956). In reasonably simple experiments, this expansion would be the most straightforward method of obtaining the missing value, and for the iterative fitting of several missing values it would appear to have a great advantage over the formulae given previously, even in more complex experiments. This is because the expansion expresses the missing value as a linear function of the other values:

in the example,

$$(2V_3 - V_1 - V_2)(S_2 - S_1)(2L_2 - L_1 - L_3) = 0,$$

and $4y = 4V_3 S_2 L_2$

$$= V_1 S_1 L_1 - V_1 S_2 L_1 - 2V_1 S_1 L_2 + 2V_1 S_2 L_2 + V_1 S_1 L_3 - V_1 S_2 L_3$$

$$+ V_2 S_1 L_1 - V_2 S_2 L_1 - 2V_2 S_1 L_2 + 2V_2 S_2 L_2 + V_2 S_1 L_3 - V_2 S_2 L_3$$

$$- 2V_3 S_1 L_1 + 2V_3 S_2 L_1 + 4V_3 S_1 L_2 - 2V_3 S_1 L_3 + 2V_3 S_2 L_3$$

DISCUSSION

Use of the general formula developed in this paper is restricted to experiments intermediate in complexity between simple factorials and those using part replicates or confounding. The simplest factorial experiments must be replicated, and the randomized block formula can be used in the treatment by replicate layout to estimate a missing value, although this may place relatively great weight on a few of the observations. If there are more than three factors, one of the formulae of the preceding section could be used. The application to complex data may be simplified if any factor is believed not to be interacting with any of the others: the data may be summed over all levels of the factor and the formula applied to the totals.

No attempt has been made to examine the effect of the calculation of a missing value on the accuracy of measurement of treatment effects, as in most cases the reduction of the number of error degrees of freedom by one is an adequate precaution. In cases of doubt, the procedure given by Cochran and Cox (1950, p. 204) may be used.

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THE DICHROMATE - LIGNOSULPHONATE REACTION AND ITS POTENTIAL USE IN CHEMICAL GROUTING

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(Received for publication, 25 September 1957)

Summary

Lignosulphonates prepared from ammonium, calcium, and sodium-based sulphite liquors have been investigated to determine their potential uses with sodium dichromate in dichromate-lignosulphonate grouting. Tests on setting time, penetration, solubility, and permeability of such mixes were carried out. The effects of curing time and addition of ferric chloride on the solubility of chromium were specially studied. These have shown that lignosulphonates derived from ammonium and calcium-based liquors have the desired properties. It is considered that field trials should be made to test the permanency of dichromate-lignosulphonate groutings.

INTRODUCTION

Lignosulphonates are by-products of the sulphite process of wood pulp production, and, since little use has been found for them they are available at low cost. Lignosulphonates are soluble in water, but when oxidised by dichromate solutions they gradually form apparently insoluble gels which have considerable strength. This property leads to the possible use of these substances in chemical grouting, in place of the usual cement or silicate grouts, or when the latter materials are unsuitable. Owing to the complexity of the reactions involved, it has not been possible to determine the mechanism by which gelation occurs. It has been suggested (Smith, 1952), however, that "the chromium coordinates with oxygen atoms in the sulphite waste possibly after oxidation of calcium lignosulphonate to form carboxylic acid groups." Cornell University has established that hexavalent chromium compounds, namely sodium and potassium dichromates, are the only practical oxidising agents for grouting (Anon.). In 1953, as a result of the U.S. Bureau of Reclamation's work a dichromate-lignosulphonate grout was used for sealing constructional leaks in the Heart Butte dam (Witte, 1957).

As the sulphite process of paper-making is not employed in New Zealand, no local supplies of lignosulphonates are available. It has been found that lignosulphonates vary greatly in their gelling properties (Anon.) and in order to determine whether this is due to the presence of different cations, lignosulphonates from ammonium- calcium- and sodium-based sulphite liquors have been examined. Tests

similar to those made by Cornell University and Bureau of Reclamation have been used in the investigation. These include setting time, stability, solubility, and penetration of the gel, for varying proportions of the individual lignosulphonates and sodium dichromate. The work has been extended to determine the effects of curing time and addition of ferric chloride on the solubility of chromium. Permeability measurements have also been made on grouted sand samples.

MATERIALS

The three lignosulphonate samples tested were:

- (1) A lignosulphonate isolated from sodium-based liquor (from Norway)
- (2) A lignosulphonate isolated from ammonium-based liquor (from Norway)
- (3) A lignosulphonate isolated from calcium-based liquor (from Sweden)

While it is appreciated that the samples are not necessarily homogeneous and may contain carbohydrates they will henceforth be referred to as sodium, ammonium, or calcium lignosulphonates respectively.

To 50% solutions of each lignosulphonate in water, varying amounts of sodium dichromate solution, ferric chloride solution and water were added. The concentrations of the sodium dichromate and ferric chloride solutions were as follows:

Sodium dichromate: 8.9 lb $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ plus 1 gal water.

Ferric chloride: 6.0 lb $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ plus 1 gal water.

The unit used was the Imperial gallon. Sodium dichromate was used in preference to the potassium compound on the basis of cost.

The solutions were mixed in the proportions given in Table 1. The order of mixing did not appear to be critical. All the grouts were prepared and the tests carried out at room temperature—i.e., approximately 70°F.

Since the initial tests showed that the dichromate-sodium lignosulphonate gels had very poor stability, later tests were restricted to the ammonium and calcium lignosulphonates.

METHOD OF TESTING

Setting Time of Grout

This was determined using a "Precision Penetrometer", manufactured by the Fisher Scientific Co., U.S.A., the needle (5 mm in diameter) and attachment of which weighed 20 g. An additional 50-g weight was loaded on to the attachment in order to obtain satisfactory

TABLE 1.—Mix Proportions.

Mix No.	Volume of component (gal. per 10 gal. lignosulphonate)			Volume ratios	
	Sodium dichromate	Ferric chloride	Water	Dichromate	Dichromate
				Ligno-sulphonate	Total components
1	2.5	—	—	0.25	0.20
2	2.0	—	—	0.20	0.17
3	1.5	—	—	0.15	0.13
4	1.0	—	—	0.10	0.09
5	2.5	1.0	—	0.25	0.19
6	2.0	0.8	—	0.20	0.16
7	1.5	0.6	—	0.15	0.12
8	1.0	0.4	—	0.10	0.09
9	1.5	0.6	1	0.15	0.11
10	1.5	0.6	2	0.15	0.11
11	2.0	—	17	0.20	0.07
12	1.5	—	2	0.15	0.11
13	2.0	—	4	0.20	0.13
14	2.0	—	8	0.20	0.10
15	2.0	—	12	0.20	0.08
16	2.0	0.8	12	0.20	0.08

penetrations during setting. The lower end of the needle (0.5 cm) was shaped in the form of a cone, so that a linear relationship did not exist between the extent of penetration and gel rigidity. The penetrometer, however, was found to provide a more useful means of following gelation than the other methods available.

The penetration of the cone of total mass 70 g in 5 sec. was noted at various times and the setting time estimated from the curve.

Penetration of Sand by Grout

Sand passing B.S.S.52 and retained on B.S.S.100 was packed in a glass tube of 4 cm diameter, with an opening at the bottom to allow the escape of entrapped air. The dichromate-lignosulphonate grout was poured on to the sand and the time required for the mix to penetrate six inches of the sand determined.

Permeability of Grouted Sand

Permeability was determined on a few selected samples of grouted sand. The samples were cylinders 1 in. thick and 3 in. in diameter. Measurements were made using a standard permeability cell in which a pressure of 75 lb/sq. in. was exerted on the sample.

Stability and Solubility of Gel

The insolubility of the dichromate-lignosulphonate gel is important because of the toxic properties of the hexavalent chromium. Further, a soluble material would not form a permanent impermeable barrier to the water flow.

TABLE 2.—Setting Times and Penetration Times of Grout.

Mix No.					Setting time	Time to penetrate 6 inches of sand (— 52 + 100 B.S.S.)
1S					1 to 2 hours	I.p.*
2S					2 to 3 hours	I.p.
3S					4 to 5 hours	50 min
4S					>7 days	92 sec
5S					$\frac{1}{4}$ to $\frac{1}{2}$ hour	I.p.
6S					$\frac{1}{2}$ to 1 hour	I.p.
7S					1 to 2 hours	I.p.
8S					10 to 15 hours	115 sec
9S					1 to 2 hours	I.p.
10S					$1\frac{3}{4}$ to $2\frac{1}{2}$ hours	I.p.
11S					>7 days (soft gel)	190 sec
1C					$\frac{1}{4}$ to $\frac{3}{4}$ hour	I.p.
2C					$\frac{1}{2}$ to 1 hour	I.p.
3C					1 to 2 hours	I.p.
4C					12 to 15 hours	I.p.
5C					$\frac{1}{4}$ to $\frac{3}{4}$ hour	I.p.
6C					$\frac{1}{2}$ to 1 hour	I.p.
7C					$\frac{3}{4}$ to $1\frac{1}{2}$ hours	I.p.
8C					$2\frac{1}{2}$ to 4 hours	I.p.
9C					$\frac{3}{4}$ to $1\frac{1}{2}$ hours	I.p.
10C					1 to 2 hours	I.p.
11C					2 to 4 days	150 sec
12C					2 to 4 hours	45 min
13C					2 to 4 hours	465 sec
14C					10 to 15 hours	240 sec
15C					20 to 30 hours	165 sec
16C					15 to 20 hours	300 sec
1A					$\frac{1}{4}$ to $\frac{3}{4}$ hour	I.p.
2A					$\frac{1}{2}$ to $\frac{3}{4}$ hour	I.p.
3A					$\frac{1}{2}$ to $1\frac{1}{2}$ hours	I.p.
4A					1 to 2 hours	I.p.
5A					$\frac{1}{8}$ to $\frac{1}{2}$ hour	I.p.
6A					$\frac{1}{8}$ to $\frac{1}{2}$ hour	I.p.
7A					$\frac{1}{4}$ to $\frac{3}{4}$ hour	I.p.
8A					1 to 2 hours	I.p.
9A					$\frac{1}{3}$ to $\frac{3}{4}$ hour	I.p.
10A					$\frac{1}{2}$ to 1 hour	I.p.
11A					2 to 4 days	135 sec
12A					$1\frac{1}{2}$ to 3 hours	I.p.
13A					$1\frac{1}{2}$ to 3 hours	720 sec
14A					4 to 10 hours	240 sec
15A					15 to 30 hours	165 sec
16A					4 to 5 hours	500 sec

I.p. = imperfect penetration

Five-gram samples of the dichromate-lignosulphonate gel (approximately 3 cm by 1.3 cm) were each shaken mechanically with 100 ml of water for 4 hr and 22 hr respectively. Since the lignosulphonates appeared to interfere with the analysis of hexavalent chromium, especially in the more concentrated solutions, the total chromium content was also determined. Oxidation with silver nitrate and potassium persulphate converted the chromium to the hexavalent state, and appeared to destroy the lignosulphonate (Hillebrand *et al.* 1953). A known volume of ferrous ammonium sulphate was then added and the excess titrated with potassium dichromate. The strong colour of the solutions in this work prevented the use of the customary diphenyl-carbazide colorimetric test for the estimation of hexavalent chromium.

The effect of time of curing of the gel and addition of ferric chloride on the concentration of soluble chromium were determined. Samples of a particular mix were also shaken for varying times up to 60 hr to determine the effect of time of contact between the gel and water on the chromium solubility.

RESULTS

The setting and penetration times are summarized in Table 2. S, C, or A is appended to the mix numbers to distinguish between the sodium-, calcium-, and ammonium-based lignosulphonates.

Permeability of Grouted Sand

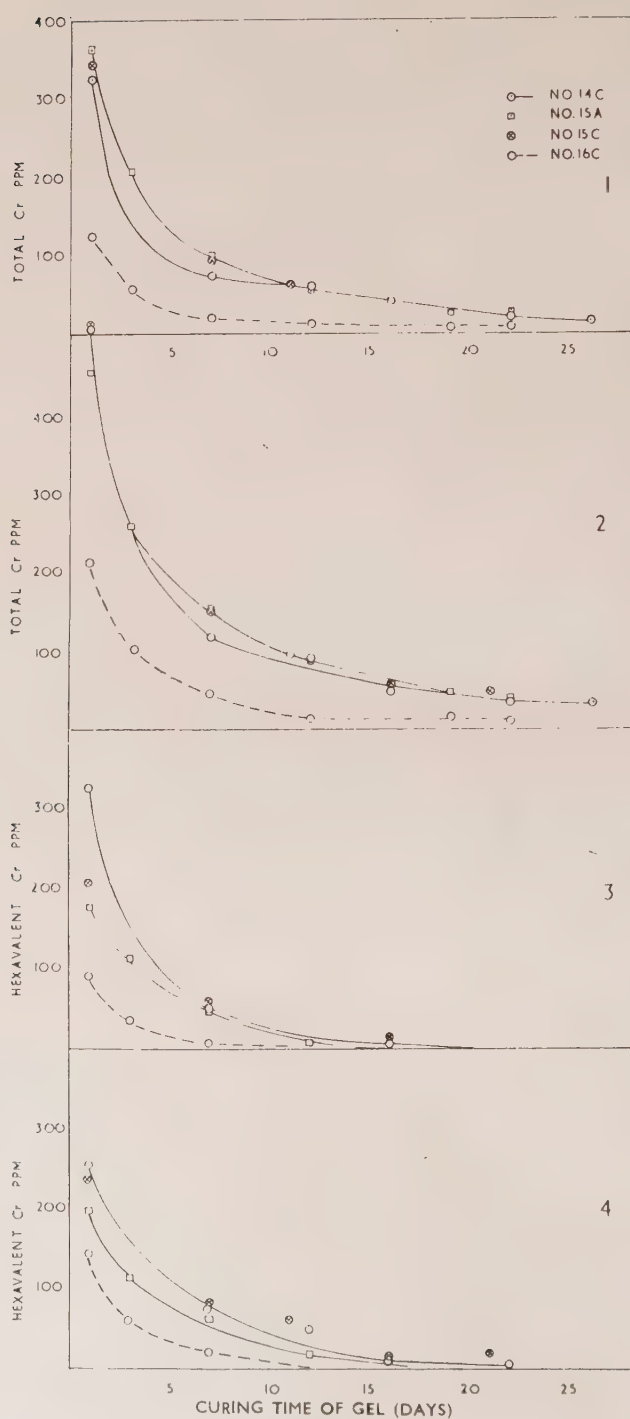
The permeability figures are given in Table 3.

TABLE 3—Permeability of Grouted Sand.

Mix No.	Permeability
13A	2×10^{-10} cm/sec
13C	3×10^{-9} cm/sec
14A	9×10^{-10} cm/sec
14C	4×10^{-7} cm/sec
15A	3×10^{-8} cm/sec
15C	4×10^{-7} cm/sec

Solubility of Gel

In Figs 1 to 4, the effects of curing time of the dichromate-lignosulphonate mixes and the addition of ferric chloride on the solubility of chromium are shown. The total chromium extracted after 4 hr and



FIGS 1, 2, 3, 4.—Graphs showing solubility of chromium with curing time and addition of ferric chloride. Nos 14C, 15A, 15C, and 16C refer to mixes given in Table 1.

22 hr is plotted in Figs 1 and 2 respectively, and the hexavalent chromium present in the same extract is given in Figs 3 and 4. Samples 14C, 15A, and 15C, which do not contain ferric chloride, are compared with sample 16C containing ferric chloride. The effect of extraction time on the solubility of chromium is shown in Fig. 5. This was determined using sample 15C cured for 12 days and subsequently ground to $-7 + 14$ B.S.S.

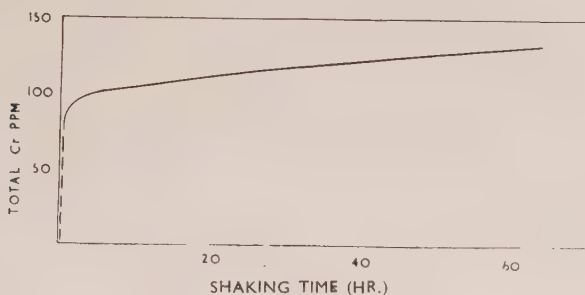


FIG. 5.—Graph showing effect of extraction time on solubility of chromium.

DISCUSSION

It will be seen from Table 2 that the gelling properties of the ligno-sulphonates vary with the cation. The dichromate-ammonium lignosulphonate grouts set more quickly than the corresponding calcium ones, which in turn set more quickly than those containing sodium lignosulphonate. While from consideration of setting time and permeability the ammonium-based grout is the most satisfactory, the resultant gel is a little less stable than the calcium product, a factor which may be insignificant in field grouting. The stabilities of the dichromate-sodium lignosulphonate gels are very poor, suggesting that this compound is unsuitable for chemical grouting.

Although a decrease in the dichromate/lignosulphonate ratio from 0.25 to 0.10 in mixes 1 to 4 results in an increase in the setting time, adequate penetration of the sand is not achieved. With a dichromate/lignosulphonate ratio of 0.20, the addition of water, changing the dichromate/total constituents ratio from 0.17 to 0.07, slows up the rate of setting and greatly improves penetration. Comparison of mix Nos. 14A and 15A shows that with the reduced overall concentration of dichromate and lignosulphonate the setting time increases from approximately 4 to 20 hours without a correspondingly large decrease in penetration time. Since 4 to 5 hours would seem to be a satisfactory setting time, it is significant that a similar time is obtained with mix No. 16A. Thus addition of ferric chloride to mix No. 15 has produced a grout (No. 16) with the desired properties of No. 14, but with 20% less dichromate and lignosulphonate by volume. As the solubility of hexavalent chromium (Figs 3 and 4) appears to be dependent upon the initial dichromate/total components ratio, and in view of the toxic

properties of hexavalent chromium, mix No. 16 would seem the most suitable of those tested for grouting. However, it might be possible to further reduce both the dichromate/lignosulphonate and dichromate/total constituents ratios without adversely affecting the gelling properties of the grout and the stability of the gel.

The figures given in Table 3 show that an increase in the proportion of water results in a small increase in the permeability. The dichromate-ammonium lignosulphonate grouted sand is less permeable than the corresponding calcium sample. It was also noted during the course of the measurements that the permeability decreased during the test, indicating a self-sealing effect.

It is apparent from Figs 1 to 4 that the curing time of the gel appreciably affects the solubility of chromium. After about 12 days, however, the effect of time becomes less significant. It will be observed that mixes 15A and 15C give almost identical results, although the gel obtained from 15A is less stable than that from 15C. The concentration of chromium extracted is reduced by the addition of ferric chloride which accelerates the dichromate-lignosulphonate reaction. However, the beneficial effect is lessened with time, becoming negligible after about 25 days' curing. The chromium solubility (Fig. 5) was also found to be dependent on the time of contact between the gel and water, the significant time being the first two hours.

It is possible that water in contact with a dichromate-lignosulphonate grouted area could dissolve enough hexavalent chromium to create a toxic hazard. However, if this water were further diluted in a river having a sufficiently large flow, the concentration of chromium downstream would not exceed the safety limit. The commonly accepted limit is that fixed by the United States Public Health Service at 0.05 ppm.

The effect of temperature on the setting time of dichromate-lignosulphonate grouts has been studied by the Cornell University (Anon.). It was shown that the setting time of a given dichromate-lignosulphonate mixture at 50°F is approximately double that for the same mixture at 70°F. Thus, suitable adjustments should be made to the proportions of components if grouting is carried out in extreme weather conditions.

Although the laboratory tests suggest that the ammonium and calcium lignosulphonates would be suitable for chemical grouting, field trials should be carried out to determine the permanency of the grouted areas and whether strength could be maintained over a long period of time.

ACKNOWLEDGEMENTS

The authors are grateful to Imperial Chemical Industries (N.Z.) Ltd. for supplying the lignosulphonate samples, Mr J. C. McDougall for assistance with the laboratory tests, Soil Bureau, D.S.I.R., for carrying out the permeability measurements, and Mr I. R. C. McDonald for helpful criticism.

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THE STEAM DISTILLATION OF VOLATILE FATTY ACIDS

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(Received for publication, 9 October 1957)

Summary

Data are presented showing the behaviour on steam distillation of a mixture of normal saturated fatty acids from formic to decanoic. It is demonstrated that the volatilities of the C_4 to C_{20} fatty acids are considerably reduced by the presence of higher molecular weight acids.

INTRODUCTION

The technique of steam distillation is established as a preparative and analytical method in fat chemistry (Morton, 1938). However, little is known regarding the behaviour of mixtures of volatile fatty acids under steam distillation. Dyer (1917), on examining the behaviour of these acids when distilled singly, found that nonanoic, the highest molecular weight acid studied, was the most volatile. However, it has been frequently observed in this laboratory that, when acids derived from natural fats are steam-distilled, C_8 to C_{10} fatty acids persist in the non-volatile residue. It appears that the volatilities of these acids are somehow affected by the presence of other acids in the mixture.

It seemed possible, therefore, that individual acids in mixtures of volatile fatty acids would behave in a manner different from single acids when steam-distilled. Indeed, Sidgwick (1920) has suggested that in mixtures of fatty acids each acid has a solubility in the others which affects the vapour pressures of each of the acids present. The advent of the gas-liquid chromatographic technique of James and Martin (1952) has made it possible to analyse quantitatively the proportions of volatile fatty acids in mixtures, and therefore it was decided to examine the behaviour of mixtures of volatile fatty acids on steam distillation.

METHODS

In the first experiment, a mixture of 0.6 millimoles of each *normal* saturated fatty acid, formic to decanoic, was steam-distilled in a micro-Kjeldahl apparatus. The acids were introduced into the apparatus as sodium salts, acidified with 40% v/v H_2SO_4 to congo red, and the volume adjusted to 35 ml with water. Steam distillation was commenced.

TABLE 1.—Percentage of Volatile Fatty Acid in Each Fraction of Steam Distillate.
Fraction No.

	1	2	3	4	5	6	7	8	9	10	% Refr.
Formic	9.1 (7.6)	10.2 (7.0)	7.5 (5.7)	6.8 (5.6)	6.0 (4.3)	4.8 (4.6)	3.3 (3.2)	2.5 (3.1)	2.4 (2.4)	2.1 (1.4)	54.7 (44.9)
Acetic	21.4 (16.1)	18.7 (12.7)	13.4 (10.9)	9.1 (9.7)	8.6 (6.9)	5.9 (4.9)	4.1 (5.7)	3.5 (4.6)	2.9 (3.8)	2.9 (3.2)	90.5 (78.5)
Propionic	35.4 (24.8)	21.4 (16.1)	12.3 (13.9)	7.3 (9.8)	4.7 (6.1)	2.9 (4.9)	1.6 (3.6)	1.7 (2.7)	1.1 (1.9)	1.1 (1.5)	89.5 (85.3)
Butyric	52.5 (34.2)	24.6 (20.6)	10.6 (15.1)	4.9 (10.0)	2.5 (5.2)	1.2 (3.9)	0.5 (2.6)	0.3 (2.3)	<0.1% (1.0)	<0.1% (0.8)	97.1 (95.7)
Valeric	66.6 (34.1)	24.8 (20.5)	8.2 (15.1)	2.8 (10.1)	1.1 (5.9)	0.5 (4.6)	0.2 (2.9)	0.1 (2.2)	<0.1% (1.2)	<0.1% (0.9)	104.3 (97.5)
Hexanoic	68.2 (24.3)	24.8 (17.6)	4.7 (14.9)	1.5 (10.7)	0.6 (7.2)	0.3 (5.8)	<0.1% (4.4)	<0.1% (3.1)	<0.1% (2.4)	<0.1% (1.9)	100.1 (92.3)
Heptanoic	61.6 (13.2)	26.0 (11.7)	8.1 (10.5)	1.5 (9.0)	0.5 (6.6)	0.1 (6.7)	0.1 (5.3)	<0.1% (4.6)	<0.1% (3.8)	<0.1% (3.6)	97.9 (75.0)
Octanoic	51.3 (7.4)	34.2 (7.0)	14.7 (7.8)	3.1 (6.0)	0.7 (5.8)	0.4 (5.9)	0.2 (5.3)	0.1 (4.5)	<0.1% (4.6)	<0.1% (4.8)	104.7 (59.1)
Nonanoic	30.8 (3.3)	30.8 (3.2)	22.4 (3.9)	7.2 (3.2)	0.9 (3.2)	0.6 (3.0)	0.4 (2.5)	0.3 (2.6)	<0.1% (2.7)	<0.1% (3.1)	93.4 (30.7)
Decanoic	17.4 (1.0)	23.5 (1.0)	27.1 (1.7)	14.6 (1.5)	1.8 (1.0)	0.8 (1.4)	0.5 (1.8)	0.2 (1.2)	<0.1% (0.7)	<0.1% (1.9)	85.9 (13.2)

Bracketed figures are those obtained when higher molecular weight acids, C₁₁ to C₁₈, are present.

and each of the 10 ml fractions collected, required an average of $2\frac{1}{2}$ min. for collection. Each fraction was titrated with standard aqueous sodium hydroxide and prepared for analysis by gas-liquid chromatography (James and Martin, 1952) as described by Hawke (1957).

The second experiment was conducted in a similar manner, but, in addition to the volatile acids, the following amounts of higher molecular weight fatty acids were included.

Myristic				1.77 millimoles
Palmitic				4.24 millimoles
Stearic				1.78 millimoles
Oleic				5.60 millimoles

RESULTS AND DISCUSSION

The composition of each 10 ml fraction is given in Table 1. The results are expressed as a percentage of the original 0.6 millimoles of each fatty acid present before steam distillation.

It can be seen from Table 1 that when the mixture of volatile fatty acids C_1 to C_{10} was steam-distilled, hexanoic was the most volatile fatty acid, 68.2% distilling in the first fraction. By comparing the volatilities in ascending series, it can be seen that the water-soluble acids, formic and acetic, have low volatilities, from propionic to octanoic are high, and those of nonanoic and decanoic are considerably lower.

The behaviour of decanoic acid is unique, in that its volatility increased as the distillation proceeded, the maximum amount distilling in fraction 3. This can be interpreted as being due to a reduction in the contribution by the fatty acids C_4 to C_7 to the lowering of the vapour pressure of decanoic acid. At fraction 3, when the suppression due to the fatty acids C_4 to C_7 has been removed, the vapour pressures of the remaining acids increase. It is interesting to note that nonanoic also shows the same tendency as decanoic acid.

Dyer (1917) found that nonanoic acid was the most volatile when steam-distilled alone, but the present work shows that, when a mixture of acids is distilled, hexanoic is the most volatile. It is clear that each acid of the mixture must reduce the volatility of the other acids present, thus confirming the validity of the theory of Sidgwick. Further support to this theory is given by the fact that, when the higher molecular weight C_{14} to C_{18} acids are present, a considerable reduction in volatility is observed for all but formic, acetic, and propionic acids, which have low volatilities even when distilled alone.

The results obtained for heptanoic acid under three conditions of distillation are shown in Fig. 1.

It can be seen that when heptanoic acid is steam-distilled in company with the mixed acids C_1 to C_{10} , the volatility is less than that observed when this acid is distilled alone. A still greater reduction in volatility

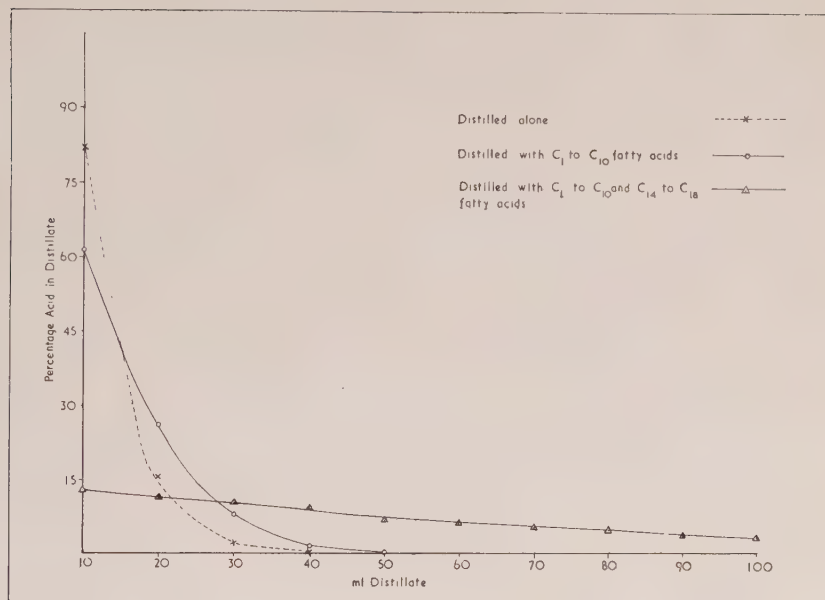


FIG. 1.—Volatility of heptanoic acid under various conditions of distillation.

is observed when the volatile fatty acids C_1 to C_{10} are steam-distilled with the higher molecular weight fatty acids C_{14} to C_{18} .

Generally, the reduction in volatility resulting from the addition of the higher molecular weight acids C_{14} to C_{18} to the mixture of volatile fatty acids C_1 to C_{10} is greatest for decanoic and least for formic. Indeed, nonanoic and decanoic acids have their volatilities so reduced that they could well be considered only slightly volatile under these conditions. It is possible that the volatile fatty acids C_1 to C_{10} partition between the aqueous phase and non-aqueous phase (droplets of C_{14} to C_{18} acids)—the C_8 to C_{10} acids in particular have a greater solubility in the non-aqueous phase. As their concentration in the aqueous phase decreases on distillation, diffusion from the non-aqueous phase results in a constant or slowly decreasing amount of these acids passing into the aqueous phase and steam-distilling. With the exception of the water-soluble acids, the bracketed figures in Table I show that, as the molecular weight of the volatile acid increases, the percentage distilling in each fraction of distillate approaches constancy. This observation is in agreement with the above-suggested explanation.

Using gas-liquid chromatography, Hawke (1957) found that when the fatty acids of New Zealand butterfat were steam-distilled until negligible quantities of fatty acids passed into the distillate, about 50% of decanoic remained in the non-volatile residue. It appears that, using steam-distillation, it is possible to separate completely the fatty acids only up to octanoic acid.

It could be expected that some variations may occur in the Reichert and Polenske values (Hopper, 1946) due to variations in the proportions of volatile to non-volatile fatty acids, high proportions giving relatively high values. In most natural fats, however, the proportion of volatile fatty acid to the total fatty acid content is small, and variations in Reichert and Polenske values, due to variations in the amount of non-volatile fatty acid, would be slight.

The results of the present work show the limitations of the older techniques for the estimation of volatile fatty acids. In connection with work on the off-flavours in butterfat, Hillig and Knudsen (1942) proposed a technique for the estimation in mixtures of volatile fatty acids up to butyric acid, whereby the sample is steam-distilled under controlled conditions and fractions are collected and titrated. In calculating the composition, the assumption is made that each acid of a mixture distils at the same rate as if it were alone. The results of the present work do not support this assumption, except for formic, acetic, and possibly propionic acids, whose volatilities are not greatly affected by the presence of higher molecular weight acids.

ACKNOWLEDGEMENT

The author expresses gratitude to Dr J. C. Hawke, of this Laboratory, for his very helpful advice, and to Dr F. B. Shorland for his continued interest in the work.

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BACTERIOLOGICAL SURVEY OF AUCKLAND HARBOURS

PART V—VERTICAL DISTRIBUTION OF SEWAGE IN WAITEMATA HARBOUR

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(Received for publication, 5 July 1957)

Summary

In the area investigated in Waitemata Harbour and under a variety of weather conditions no regular stratification of sewage occurred. After considering several possibilities it is suggested that tidal movement over an uneven bottom causes vertical eddies which are responsible for mixing. Postulated methods of dispersal of sewage-polluted water by wind and tide are reconsidered. The pollution appears to be greater than previously suggested but it is not cumulative. Determination of M.P.N. (most probable number) coliform organisms is recommended as being the most sensitive and satisfactory method for studying the pollution of waterways by sewage.

INTRODUCTION

The vertical distribution of polluting material in waterways is of fundamental importance. Previous work (Wallace *et al.*, 1953a, b, 1954, 1956) was based on samples taken only in the top three feet of water.

During the investigations previously reported (Wallace *et al.*, 1953a, b) commercial dredging for edible mussels was commenced north-east of North Head in Waitemata Harbour, in the vicinity of sample stations E 897, E 1115, E 1065 (Fig. 1), but was prohibited after some of the results reported herein and earlier (Wallace *et al.*, 1953a, b) were considered.

The investigation discussed in this paper was limited to waters in the vicinity of the Orakei sewage outfall and northward along the Rangitoto channel for some miles.

Sampling was carried out between 12 June 1953 and 5 April 1954.

METHODS

Depth samplers are described in the literature (Thresh *et al.*, 1949, Stowe and Teeple, 1951, Whipple, 1927, Woodward, 1948, Zobell, 1946). The sampler used was an evacuated bottle which could be opened at the

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required depth, so that the depth at which the sample was taken was positively known. Samples were taken from the deck of Marine Department launches which were allowed to drift during sampling. The location of the vessel at the commencement and finish of sampling and its approximate course during this period were plotted (Fig. 1). The samples were examined as in previous investigations (Wallace *et al.*, 1953a, b, 1954).

RESULTS

Results are presented for individual sampling stations in the following tables. Except where modified in the text the location refers to the sampling stations shown in Figs 1 and 2.

Figure 2, on the same horizontal scale as Fig. 1, is a three dimensional presentation of the most probable number of coliform organisms per 100 ml of sample at the various sampling stations which are indicated by the vertical lines and identified by the sample numbers along the lower edge of the map. The depths indicated are from low tide level.

DISCUSSION

One of the most important findings of this investigation was the fairly even vertical distribution of bacteria. It has been previously suggested (Wallace *et al.*, 1953a) that stratification of the sewage occurs after discharge, the sewage being concentrated in the surface layers and that these sewage-rich layers are transported by wind and tide to extend or limit the area polluted. This investigation has shown only three series of samples, E 995, E 1035, and E 1065, in which the concentration is greatest near the surface. Even with these there were fewer organisms in the surface layer than at one fathom. In Fig. 2 it will be seen that there is no regular distribution of coliform bacteria through the water.

These samples were taken under a variety of weather, tidal, and sewage-discharge conditions.

From these results it is concluded that, notwithstanding the higher temperature and lower density of the discharged sewage in comparison with the receiving waters, there is a fairly rapid dispersion of the polluting material through the whole depth of the harbour waters and as a consequence the pollution of the water as a whole is considerably greater than was envisaged previously when pollution of only the surface layers was postulated.

An explanation of this even distribution must be sought from consideration of possible contributing factors, (a) rapid sedimentation of the sewage, (b) a much greater efficiency of mixing of the sewage discharged from a single opening into the receiving water than was accepted previously, (c) a much greater mixing of the whole of the

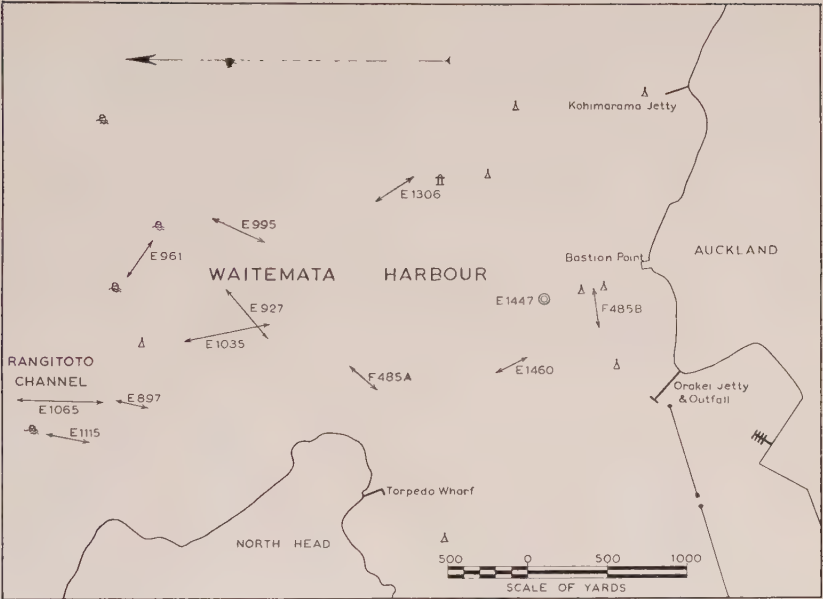


FIG. 1.—Sampling Stations in Waitemata Harbour.

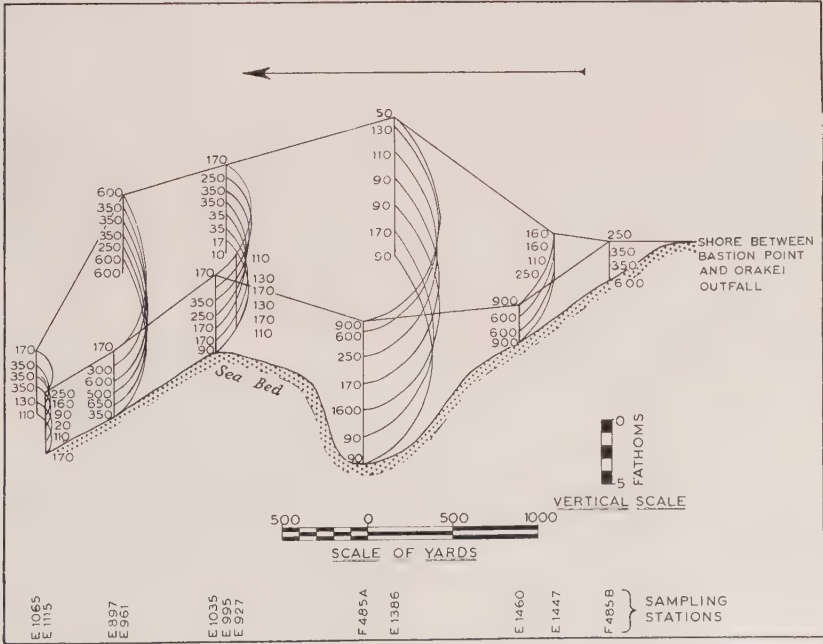


FIG. 2.—Three-dimensional illustration of distribution of coliform organisms over sampling area

RESULTS FROM DEPTH SAMPLES WAITEMATA HARBOUR

Location: E. 805. Off end of Princes Wharf. Date: 12/6/53.

High Tide: 7.50 a.m.

Sewage discharge: Partial discharge up to 10.38 a.m. after which full discharge.

Time first sample taken: 11.23 a.m.

Weather: Heavy showers previous few days. South-westerly winds Force 1, light occasional showers on day of sampling.

Distance from surface in fathoms.	M.P.N. coli/100 ml.	N.A. 37°C count/ml.	N.A. 22°C count/ml.	Coli/IAC Ratio	Coliform types isolated	<i>C. welchii</i>	Chlorides /100,000
4	350	93	180	4:5	<i>E. coli</i> I	+	1804
3	900	117	195	5:4	<i>E. coli</i> I and Irregular I	+	1815
1½	900	108	186	5:3	<i>E. coli</i> I	+	1811
Surface	350	90	20	3:4	<i>E. coli</i> I	+	1804

Location: E. 826. Off end of Princes Wharf. Date: 15/6/53.

High tide: 10.12 a.m.

Sewage discharge: Discharging between 11.34 p.m. 14/6/54 and 5.26 a.m.

Time first sample taken: 11.20 a.m.

Weather: Showery, mainly northerly winds for previous few days and on day of sampling.

Distance from surface in fathoms.	M.P.N. Coli/100 ml.	N.A. 37°C count/ml.	N.A. 22°C count/ml.	Coli/IAC Ratio	Coliform types isolated	<i>C. welchii</i>	Chlorides /100,000
4½	1600	100	100	3:5	<i>E. coli</i> I	+	1843
3½	350	80	107	5:4	<i>E. coli</i> I	+	1818
2½	1800+	70	102	4:5	<i>A. aerogenes</i> I	+	1829
1½	600	107	183	5:5	Intermediate I	No test	1778
Surface	900	100	134	5:4	<i>E. coli</i> I	+	1739

Location: E. 897 (See Fig. 1). Date: 29/6/53.

High tide: 9.00 a.m. Surface temp.: 13.8°C.

Sewage discharge: Partial discharge up to 11.35 a.m. After which full discharge.

Time first sample taken: 11.12 a.m.

Weather: Heavy showers previously but fine with southerly winds on day of sampling.

Distance from surface in fathoms	M.P.N. Coli/100 ml.	N.A. 37°C count /ml.	N.A. 22°C count /ml.	Coli /IAC Ratio	Coliform types isolated	<i>C. welchii</i>	Chlorides /100,000
4½	350	15	21	5:4	<i>E. coli</i> I	+	1884
3½	650	18	28	4:4	<i>E. coli</i> I	—	No test
2½	500	24	60	5:3	<i>E. coli</i> I	+	No test
1½	600	24	41	5:4	<i>E. coli</i> I	—	No test
¾	300	96	52	3:5	<i>E. coli</i> I	+	No test
Surface	170	45	42	4:5	<i>E. coli</i> I	+	1880

Location: E. 927. Date: 2/7/53.

High tide: 11.28 a.m.

Sewage discharge: No details.

Time of first sample taking: 12.10 p.m.

Weather: Showery with light and variable winds.

Distance from surface in fathoms	M.P.N. Coli/100 ml.	N.A. 37°C count /ml.	N.A. 22°C count /ml.	Coli /IAC Ratio	Coliform types isolated	<i>C. welchii</i>	Chlorides /100,000
5½	110	7	36	4:4	<i>E. coli</i> I	+	1888
4½	170	12	48	5:3	<i>E. coli</i> I	+	1888
3½	130	7	38	4:2	<i>E. coli</i> I	—	1880
2½	170	14	39	4:4	<i>E. coli</i> I	+	1888
1½	130	5	30	4:4	<i>E. coli</i> I	—	1895
Surface	110	4	28	3:2	<i>E. coli</i> I	—	1899

Location: E. 961. Date: 7/7/53.

Low tide: 9.43 a.m. Surface temp.: 13.7°C.

Sewage discharge: Partial discharge up to 6.44 a.m., after which full discharge.

Time first sample taken: 11.20 a.m.

Weather: Showery weather with light and variable winds on day of sampling; 4 in. of rain fell on night of 4th July.

Distance from surface in fathoms	M.P.N. Coli/100 ml.	N.A. 37°C count /ml.	N.A. 22°C count /ml.	Coli/IAC Ratio	Coliform types isolated	<i>C. welchii</i>	Chlorides /100,000
6	600	34	86	4:5	<i>E. coli</i> I	+	1838
5	600	39	78	3:5	<i>E. coli</i> I	+	1835
4	250	42	72	5:4	<i>E. coli</i> I	+	1838
3	350	30	106	5:3	<i>E. coli</i> I	+	1835
2	350	90	171	4:5	<i>E. coli</i> I	+	1795
1	350	50	156	4:5	<i>E. coli</i> I and <i>A. aerogenes</i> I	+	1792
Surface	600	60	173	4:4	<i>E. coli</i> I	+	1795

Location: E. 995. Date: 14/7/53.

High tide: 9.49 a.m. Surface temp.: 12.7°C.

Sewage discharge: No discharge for previous 5 hours.

Time first sample taken: 10.04 a.m.

Weather: Continuous heavy rain for several days. More or less fine previous two days. Winds light westerly.

Distance from surface in fathoms	M.P.N. Coli/100 ml.	N.A. 37°C count /ml.	N.A. 22°C count /ml.	Coli/IAC Ratio	Coliform types isolated	<i>C. welchii</i>	Chlorides /100,000
6	10	8	21	5:1	Intermediate I	+	1913
5	17	8	27	2:2	<i>E. coli</i> I	+	1904
4	35	11	36	5:1	<i>E. coli</i> I	+	1891
3	35	12	41	5:3	<i>E. coli</i> I	—	1894
2	350	21	25	4:3	Irregular I	—	1870
1	250	32	37	5:4	<i>E. coli</i> I	+	1852
Surface	170	25	32	4:5	<i>E. coli</i> I	—	1852

Location: E. 1035. Date: 21/7/53.
 Low tide: 8.30 a.m. Surface temp.: 13°C.
 Sewage discharge: Full discharge 7.05 a.m. to 11.35 a.m.
 Time first sample taken: 11.45 a.m.
 Weather: Nor' westerly winds Force 3 with occasional showers. Previous weather westerly winds, occasional showers.

Distance from surface in fathoms	M.P.N. Coli/100 ml.	N.A. 37°C count /ml.	N.A. 22°C count /ml.	Coli /IAC Ratio	Coliform types isolated	<i>C. aerichii</i>	Chlorides /100,000
6	90	23	28	5:4	<i>E. coli</i> I	+	1862
5	170	18	25	5:2	<i>E. coli</i> I	+	1858
4	170	23	32	5:4	<i>E. coli</i> I	+	1858
3	250	11	23	5:4	<i>E. coli</i> I	+	1858
1½	350	22	16	4:4	<i>E. coli</i> I	+	1858
Surface	170	29	700	5:3	<i>E. coli</i> I	+	1854

Location: E. 1065. Date: 28/7/53.
 High tide: 7.50 a.m. Surface temp.: 12.9°C.
 Sewage discharge: No discharge for previous 5 hours.
 Time first sample taken: 9.58 a.m.
 Weather: Westerly showers for previous few days. Fine and cold with light sou'-westerly winds on day of sampling.

Distance from surface in fathoms	M.P.N. Coli/100 ml.	N.A. 37°C count /ml.	N.A. 22°C count /ml.	Coli /IAC Ratio	Coliform types isolated	<i>C. aerichii</i>	Chlorides /100,000
5	110	17	35	3:4	<i>E. coli</i> I	+	1894
4	130	16	31	5:5	<i>E. coli</i> I and <i>A. aerogenes</i> I	—	1894
3	350	16	23	5:4	<i>E. coli</i> I	—	1894
2	350	12	38	4:3	<i>E. coli</i> I	+	1888
1	350	22	35	4:3	<i>E. coli</i> I	—	1888
½	600	28	45	5:3	<i>E. coli</i> I	+	1888
Surface	170	27	23	4:4	<i>E. coli</i> I	—	1877

Location: E. 1115. Date: 4/8/53.

High tide: 2.44 p.m. Surface temp.: 12.5°C.

Sewage discharge: Full discharge 5.16 a.m., closed to partial discharge around 9.30 a.m.

Time first sample taken: 1.43 p.m.

Weather: Fine and cold with light sou'-westerly winds for previous week. Northerly winds Force 3 on day of sampling and for previous 24 hrs. Light showers on day of sampling.

Distance from surface in fathoms	M.P.N. Coli./100 ml.	N.A. 37°C count /ml.	N.A. 22°C count /ml.	Coli./IAC Ratio	Coliform types isolated	<i>C. welchii</i>	Chlorides /100,000
6	350	10	24	3:2	<i>E. coli</i> I	...	1887
5	170	10	31	5:3	<i>E. coli</i> I	...	1887
4	110	12	25	5:3	<i>E. coli</i> I	...	1884
3	20	10	9	4:3	<i>E. coli</i> I	...	1881
2	90	11	37	5:2	<i>E. coli</i> I	...	1887
1	160	15	31	5:2	<i>E. coli</i> I	...	1894
Surface	250	28	68	5:1	<i>E. coli</i> I	...	1887

Location: E. 1386. Date: 7/9/53.

High tide: 6.59 a.m.

Sewage discharge: Partial discharge up to 9.46 a.m., after which full discharge.

Time first sample taken: Noon.

Weather: Nor'-westerly winds with occasional light showers for previous few days. Heavy showers, with westerly winds, Force 4, on day of sampling.

Distance from surface in fathoms	M.P.N. Coli./100 ml.	N.A. 37°C count /ml.	N.A. 22°C count /ml.	Coli./IAC Ratio	Coliform types isolated	<i>C. welchii</i>	Chlorides /100,000
11	90	30	29	4:2	<i>E. coli</i> I	...	1900
9	170	32	40	4:1	<i>E. coli</i> I	...	1857
7	90	20	18	4:1	<i>E. coli</i> I	...	1849
5	90	30	26	4:1	<i>E. coli</i> I	...	1823
3	110	27	25	4:2	<i>E. coli</i> I	...	1815
1	130	27	26	4:1	<i>E. coli</i> I	...	1823
Surface	50	40	40	4:1	<i>E. coli</i> I	...	1819

Location: E. 1447. Date: 5/10/53.

High tide: 5.40 a.m.

Sewage discharge: Partial discharge up till 5.36 a.m., after which full discharge.

Time first sample taken: 10.55 a.m.

Weather: South-westerly winds, Force 4, on day of sampling and for previous day.

Distance from surface in fathoms	M.P.N. Coli/100 ml.	N.A. 37°C count /ml.	N.A. 22°C count /ml.	Coli /IAC Ratio	Coliform types isolated	<i>C. welchii</i>	Chlorides /100,000
4	1800+*	1260	1390	5:5	<i>E. coli</i> I, Intermediate I, Irregular I	+	1891
3	250	14	10	4:3	<i>E. coli</i> I, Intermediate I	+	1910
2	110	21	15	3:3	<i>E. coli</i> I	+	1901
1	160	28	12	3:3	<i>E. coli</i> I, Irregular I	+	1901
Surface	160	17	15	3:4	<i>E. coli</i> I	—	1901

* This sample contained some sediment from the sea-bed.

Location: E. 1460. Date: 7/10/53.

High tide: 7.12 a.m.

Sewage discharge: Full discharge 9.00 a.m. to 1.18 p.m., after which partial discharge.

Time first sample taken: 2.18 p.m.

Weather: Westerly winds on day of sampling, but north-easterly the previous day and mainly westerly winds for previous week. Occasional showers for previous two days.

Distance from surface in fathoms	M.P.N. Coli/100 ml.	N.A. 37°C count /ml.	N.A. 22°C count /ml.	Coli /IAC Ratio	Coliform types isolated	<i>C. welchii</i>	Chlorides /100,000
3	900	53	114	5:4	<i>E. coli</i> I and Intermediate I	—	1917
2	600	45	123	4:5	<i>E. coli</i> I	—	1921
1	900	50	110	5:5	<i>E. coli</i> I	+	1914
Surface	600	39	126	4:4	<i>E. coli</i> I	+	1917

Location: F. 485 A & B. Date: 5/4/54.

High tide: 8.48 a.m.

Sewage discharge: Full discharge 5.48 a.m.

Time first sample taken: A. 10.38 a.m., B. 11.23 a.m.

Weather: Fair to cloudy with moderate to fresh south-westerly winds for previous few days and west to south-west winds on day of sampling.

Distance from surface in fathoms	M.P.N. Coli/100 ml.	N.A. 37°C count/ml.	N.A. 22°C count/ml.	Coli/IAC Ratio	Coliform types isolated		<i>C. welchii</i>	Chlorides /100,000
					<i>E. coli</i> I	<i>E. coli</i> II and <i>A. aerogenes</i> I		
A. 11	90	22	19	4:2	<i>E. coli</i> I	...	+	1984
9	90	25	27	4:3	<i>E. coli</i> I	...	-	1973
7	1600	22	23	3:4	<i>E. coli</i> I	...	-	1981
5	170	22	20	4:4	<i>E. coli</i> I	...	-	1981
3	250	24	30	4:3	<i>E. coli</i> I	...	-	1981
1	600	26	39	4:3	<i>E. coli</i> I	...	-	1981
Surface	900	27	22	4:3	<i>E. coli</i> I	...	No test	No test
B. 5	600	59	52	4:3	<i>E. coli</i> I and Irregular II	...	-	1981
4	350	39	68	4:4	<i>E. coli</i> I	...	+	1973
3	600	66	78	4:4	<i>E. coli</i> I and Irregular II	...	-	1981
2	350	63	63	4:4	<i>E. coli</i> I	...	-	1973
1	350	60	64	4:4	<i>E. coli</i> I	...	+	1981
Surface	250	44	33	4:4	<i>E. coli</i> I	...	+	1981

receiving waters as a result of tidal movement over an uneven bottom in relatively shallow depths.

If sedimentation were the dominant factor then, at a distance of 3,500 yards from the point of discharge (samples E 961 and E 897), it would be reasonable to expect a gradation in the distribution of coliform organisms with increased numbers near the bottom and few organisms near the surface.

It is suggested that the movement of water over an uneven sea bottom under the influence of tides is probably primarily responsible for the intermixing that has occurred. In Fig. 2 the sea bottom is shown to be irregular in the area under investigation and vertical eddying could take place.

The formation of a highly polluted surface layer in this vicinity has been disproved. It is therefore necessary to modify the previous conclusions (Wallace *et al.*, 1953a, b) concerning the effect of wind and tide on the transport of polluted water. Except for sample F 485 A & B, the chlorinity of the water in the area covered by these samples was consistently lower than that found (Wallace *et al.*, 1953b, 1954) in more distant parts of the harbour which were not polluted. The density of this polluted water is less and so it would tend to rise over the more dense unpolluted water under the effect of wind and tide.

The bacterial counts on nutrient agar after incubation at 37°C and at 22°C generally followed the trend of the M.P.N. coliform organisms. The chlorinity did not always indicate dilution of sea water when high coliform counts were observed, nor did it follow the pattern set by the coliform count.

In a previous paper (Wallace *et al.*, 1953b) it was shown that serious pollution will persist up to 5½ hours after the harbour was polluted by sewage discharge. Samples taken at E 1065 confirm this but even though this does occur a very rapid rate of purification, must generally be the case, for there is no evidence that pollution builds up beyond a certain maximum level despite daily discharge of highly polluting sewage. Similar conclusions have been deduced regarding both Manukau Harbour (Wallace *et al.*, 1956) and Tamaki River and Estuary (Wallace *et al.*, 1954). The method of purification is not clear. The concentration of predatory micro-organisms found during an earlier investigation of the area (Wallace *et al.*, 1953a) was not as high as it was in Tamaki River and Estuary (Wallace *et al.*, 1954) where they were considered important factors in the process of purification, and, because of the depth of the water, the area could not be effective as an oxidation pond as was postulated for Manukau Harbour (Wallace *et al.*, 1956).

In this as in previous investigations the M.P.N. coliform organisms per 100 ml of sample is considered by the author to be a most sensitive and consistent measure of pollution and it is recommended that in further investigations on harbour pollution from sewage discharge other estimations, both chemical and bacteriological, are unnecessary.

ACKNOWLEDGEMENTS

Thanks are expressed for the co-operation of Mr Gilliver, chief inspector, and inspectors of the Fisheries Section of the Marine Department, Auckland, who provided launch facilities and assistance with sampling; to Mr P. Hutcheson, Auckland Harbour Board, for details of the conformation of the sea bed, Waitemata Harbour; to Mr B. Teehan for final drafting of figures; to Mr R. Hicks, Auckland Metropolitan Drainage Board, for details of sewage discharge; to Mr K. M. Griffin, Government Analyst, Auckland, for helpful direction; and to the Director, Dominion Laboratory for permission to publish.

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OPTIMUM ARRAYS FOR DIRECTION FINDING

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(Received for publication, 8 October 1957)

Summary

Incoherent waves that come from a distributed source may be thought of as being the sum of innumerable coherent wave trains whose directions and wavelengths differ. The paper concerns the design of an array of receivers that is intended to explore the distribution of wave power with wave direction. It is shown possible to realise in practice arrays which determine the distribution of power with the minimum mean square error that is theoretically possible. Various examples are discussed.

INTRODUCTION

Waves that have a natural origin are usually incoherent. Waves generated on the sea by wind are an example. Radio waves that come from sources outside the earth are another. Such waves may be thought of as being the sum of innumerable sinusoidal wave-trains travelling in different directions and having different wavelengths. Such waves are best described by a plot showing how the wave power varies with wave direction and with wavelength (or wave number). This is a directional power spectrum. It is easy to select waves of a certain frequency, and therefore of a certain wavelength, by using sharply-tuned receivers. This paper is concerned with the method of measuring the directions of the waves selected in this way.

The directional properties of the incoherent wave can be explored by using a directional receiver. A single receiver may not have any marked directional qualities, but it is well known that a number of receivers can be set out as a spaced array which is very sensitive to the direction of wave travel.

An alternative method (Barber, 1954) estimates the directional spectrum of the waves from the correlation coefficients observed between detectors set at various separations. The early part of this paper explains how an array gets its directional properties, and incidentally it shows that the output of an array can quite naturally be written as the sum of a number of values of the space correlogram of the waves. Consequently, the examinations of a wave system by means of a directional array or by means of correlation measurements are not to be thought of as having different basic principles but as being merely different techniques of deriving the same answer.

The correlation method mentioned above leads to the directional spectrum through a formula which is in fact the sum of the first N terms of the Fourier series representing the spectrum. As Arsac (1956)

has pointed out, such a formula has a smaller mean square error than has any other formula that uses only the harmonics up to the N th order. This formula will be called the "optimum" description of the directional spectrum of the waves. A formula, however, is inconvenient because it calls for much computational work on the part of the experimenter before the spectrum can be pictured as a curve. On the other hand, directional arrays produce a curve approximating to the directional spectrum without such numerical work. Since directional arrays act by a principle essentially the same as that used in correlation analysis it is to be expected that a suitably designed array could also provide the "optimum" curve, and would do so without requiring numerical work on the part of the experimenter.

The need for the "optimum" representation has been recognised by Bracewell (1955) who has devised methods of processing the measured curve provided by a uniform array so that it becomes closer to the "optimum" curve. Arsac (1956) has recently drawn attention to the existence of this optimum way of representing the directional spectrum, but except in rather simple instances he has not shown how it can be achieved by a directional array.

The later part of this paper shows certain systems by which arrays can be designed to give this optimum representation of the directional spectrum. Such arrays are peculiar in that their polar diagrams possess numerous side lobes which are alternately of positive and negative sign. Curve A of Fig. 6 is a typical example.

It is interesting to note that one example of an "optimum" array is already in use. This is the Mills cross (Mills and Little, 1953). The numerous side-lobes of its polar diagram would make it unsuitable for work in radio astronomy where many point-sources have to be resolved, and in practice Mills and Little attenuate the side lobes by weighting the receivers in a special way. This process in effect destroys the "optimum" qualities of the array.

THE DIRECTIONAL POWER SPECTRUM

The direction of travel of a wave is best described as being that direction in space along which the rate of change of phase with distance is a maximum. It would be easy to deduce the wave direction and also the wavelength, if the components of this gradient could be measured along three rectangular axes, or along two rectangular axes in the case of a surface wave. For instance, in the two-dimensional case, if l and m were the phase gradients measured in cycles per unit distance along the x and y axes, the total gradient would be k and the wavelength would be $1/k$ where

$$k = + (l^2 + m^2)^{\frac{1}{2}} \quad \dots\dots\dots (1)$$

The direction of the line of travel would be at θ to the normal to the x axis where

$$l = k \sin \theta \quad , \quad m = k \cos \theta \quad \dots\dots\dots (2)$$

A line-array of receivers can measure the phase gradient of the wave only in the direction of that line upon which the receivers lie. Thus, if the receivers lie on the x axis they can measure gradient l . With radio waves or with gravity waves on water it is possible also to infer the value of k from observation of the wave frequency; the angle θ can then be deduced from equation 2. This final step is not always possible. For instance, with seismic waves the elastic properties of the ground may vary considerably and on a new site the relation between frequency and wavelength, that is the wave velocity, cannot be predicted before the experiments begin. For the present purpose it is best to continue to work in terms of the measured phase-gradient l and to leave the wave direction to be deduced at a later stage. It will be seen, however, from equation 2 that the gradient l is proportional to the sine of the angle of incidence θ . A wave with zero gradient is one that is incident normally on the array.

A random wave is best described not by its amplitude and phase, but by its power, which is the mean square of the displacement the wave produces. A random wave may be thought of as being the sum of innumerable coherent trains which travel in various directions and it is necessary to describe how the power is apportioned among these various trains. The trains are being distinguished by their different phase gradients, l , and it is appropriate to express the wave power as a function of l . Let

$$E(l) . \delta l$$

be the total power of all the trains with gradients in the range l to $l + \delta l$. Then $E(l)$ is a power density and regarded as a function of l it is a power spectrum. The aim of the array is to measure this power spectrum.

There is a well-known relation between the power spectrum $E(l)$ and the space correlogram of the wave system along the x axis. The two are Fourier transforms (Khinchine, 1934; Rice, 1944; Bartlett, 1955). Thus, if there are two receivers of unit sensitivity at points x and $x + X$, giving signals $u(x, t)$ and $u(x + X, t)$, the time-averaged mean product of these signals is the value of the space correlogram for the interval X . It does not depend upon the precise position of the receivers, but only on their separation.

$$\overline{u(x, t) . u(x + X, t)} = \rho(X) \quad \dots\dots\dots (3)$$

Its relation to the power spectrum is

$$\rho(X) = \int_{-\infty}^{\infty} E(l) \cdot \cos 2\pi lX \cdot dl \quad \dots\dots\dots (4)$$

A LINE ARRAY AND ITS GAIN CURVE

Suppose that K receivers are set at positions $x_1, \dots, x_K$ upon the x axis, and suppose that the incoming waves cause them to give signals $v_1(t), \dots, v_K(t)$. The signals are added to give a total signal $V(t)$.

$$V(t) = \sum_1^{r=K} v_r(t)$$

The power of this total signal, that is its mean square, is measured and averaged over a time long enough to give a value that is statistically reliable. The power is

$$\text{Power} = \overline{V^2} = \sum_1^{r=K} \sum_1^{s=K} \overline{v_r \cdot v_s} \quad \dots\dots\dots (5)$$

This expression shows that the measured power is the sum of many terms, a typical one, $\overline{v_r \cdot v_s}$ being the time-averaged mean product of the signals from the receivers at positions x_r and x_s . If the receivers have unit sensitivity this mean product is a value of the space correlogram, namely $\rho(x_r - x_s)$. If the detectors have sensitivities b_r and b_s this introduces a factor $b_r \cdot b_s$. Then

$$\overline{v_r \cdot v_s} = b_r b_s \cdot \rho(x_r - x_s) \quad \dots\dots\dots (6)$$

The power output of the array of K receivers is therefore the sum of a number of suitably weighted values of the space correlogram of the waves. It is not surprising, therefore, that the power spectrum of the wave system may be found either by using an array of receivers in the manner now being discussed or, alternatively, by measuring separately certain values of the space correlogram and combining them in a suitable way (Barber, 1957).

To continue, equations (4) and (6) allow the power output of the array to be written in terms of the power spectrum. Equation (5) becomes

$$\text{Power} = \int_{-\infty}^{\infty} E(l) \cdot \sum_{r=1}^{r=K} \sum_{s=1}^{s=K} b_r b_s \cdot \cos 2\pi l(x_r - x_s) \cdot dl \quad \dots\dots\dots (7)$$

This equation shows that the power output of the array is a weighted integral of the whole power spectrum, that is the output depends to some extent on all the waves that are present, whatever their direction. However, the weighting function is

$$g(l) = \sum_{r=1}^{r=K} \sum_{s=1}^{s=K} b_r b_s \cdot \cos 2\pi l(x_r - x_s) \quad \dots\dots\dots (8)$$

It is the sum of many cosine terms. When l is zero the cosines are all unity and the weighting function is a maximum. For other values of l the sum is smaller. Indeed, with an extensive array having many detectors the weighting function $g(l)$ may be insignificantly small, except for values of l in quite a small range about zero. Such an array gives good discrimination because its power output is due dominantly to those waves whose directions of travel lie within a small angle about the normal to the array.

The function $g(l)$ will be called the "gain curve" of the array. If it were plotted against the angle of wave incidence, θ , instead of against l it would be the "polar diagram" of the array.

Arsac has given an expression for the gain curve similar to equation (8). He starts with knowledge that the gain curve of the amplitude of a transmitted signal is the Fourier transform of the current distribution in the transmitting aerial. He squares this gain curve to obtain the gain curve for transmitted power and applies the result to a receiving system.

The gain curve of an array can easily be calculated from equation (8) when the positions and sensitivities of the receivers are known. It is perhaps of interest to illustrate this by two simple examples. The examples do not involve many receivers and in consequence the gain curves do not possess the narrow central peak which is necessary if an array is to give an accurate measure of the directional spectrum.

Fig. 1 (a) shows three receivers of unit sensitivity set at positions O, D, and 2D. Because there are three detectors there are nine terms in the gain curve given by equation (6). In three of these terms the digits r and s are equal so the interval $(x_r - x_s)$ is zero. In two terms the interval is D and in two others it is $-D$, in one term the interval is $2D$ and in another it is $-2D$. The gain curve is therefore

$$g(l) = 3 + 2(2 \cos 2\pi lD + \cos 4\pi lD) \quad \dots\dots\dots (9)$$

and this is plotted in Fig. 1 (c).

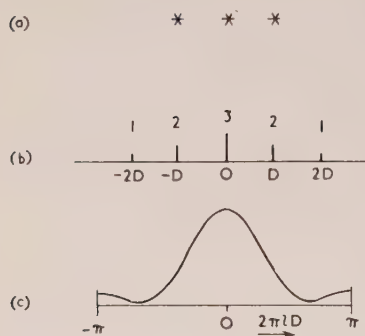


FIG. 1. A set of three receivers (a) and their gain curve (c) $g(l) = 3 + 2(2 \cos 2\pi lD + \cos 4\pi lD)$. The spectrum of this gain curve is the convolution of the array (b).

This formula can also be got by a slightly different procedure. Given the form of the array of receivers, plot the various space intervals which each receiver presents to others and to itself. Each interval should be weighted by the product of the sensitivities of the receivers that produce it, though in the present example the sensitivities are all unity. If the same interval is presented more than once its weights are added. The resulting pattern is the "convolution" of the array. In the present example the array (a) has the convolution shown in (b). This convolution is the spectrum of the gain curve, which can therefore be written down as

$$\begin{aligned} g(l) &= e^{-i4\pi lD} + 2e^{-i2\pi lD} + 3 + 2e^{i2\pi lD} + e^{i4\pi lD} \\ &= 3 + 2(2 \cos 2\pi lD + \cos 4\pi lD) \end{aligned}$$

As another example, Fig. 2 (a) shows three detectors of unit sensitivity set at positions O, D, and 3D. Fig. 2 (b) plots the set of inter-

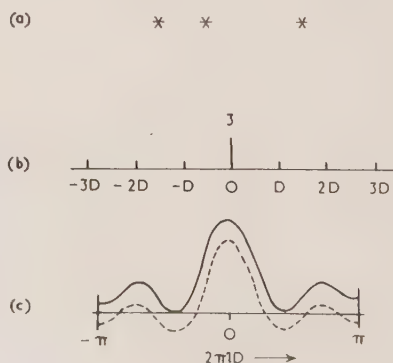


FIG. 2.—A set of three receivers (a) and their gain curve (c) $g(l) = 3 + 2(\cos 2\pi lD + \cos 4\pi lD + \cos 6\pi lD)$. The spectrum of this gain curve is the convolution of the array, (b). The broken curve in (c) is an "optimum" gain curve got by subtracting a constant from the power output of the array.

vals presented by the array, in other words its convolution. From this it is easy to see that the gain curve must be

$$g(l) = 3 + 2(\cos 2\pi lD + \cos \pi 4lD + \cos 6\pi lD) \dots\dots\dots (10)$$

This curve is pictured as the full line in Fig. 2 (c).

An array can be used to measure the power of waves coming from directions other than the normal. This is done by introducing different time delays or different phase shifts into the various signals before they are added. For instance, a typical sinusoidal wave having a frequency f and travelling in a direction defined by l gives rise to the following signals.

$$a \cos 2\pi (lx + ft) \quad , \quad x = x_1, \dots\dots x_K$$

If phase reductions equal to $l_0x_1, \dots\dots l_0x_K$ are introduced into the various signals they become

$$a \cos 2\pi ((l - l_0)x + ft) \quad , \quad x = x_1, \dots\dots x_K$$

The whole of the previous argument can then be repeated to show that the power output of the array is an integral of the power spectrum, weighted this time by the function $g(l_0 - l)$.

$$P(l_0) = \int_{-\infty}^{\infty} E(l) . g(l_0 - l) dl \dots\dots\dots (11)$$

This weighting is greatest when $(l_0 - l)$ is zero, so the array is accepting waves from a direction defined by

$$l = l_0$$

The output of the array is then an approximate measure of the power density of these waves, namely $E(l_0)$.

By repeating the measurements with phase delays corresponding to many different values of l_0 the whole range of directions can be examined and a curve produced which approximates to the true directional spectrum. The accuracy of the result depends on the weighting function $g(l)$ that is characteristic of the array.

A CRITERION FOR THE PERFORMANCE OF AN ARRAY

When an array is set to measure the power of waves with some phase gradient l_0 its power output $P(l_0)$ is only an approximation to the

actual power density $E(l_0)$. Arsac has suggested that the aim in designing an array should be to make the error.

$$E(l_0) - P(l_0)$$

have the smallest mean square when averaged over the whole range of l_0 .

Briefly, his solution is as follows. If none of the waves that are present has a wavelength less than some value L , then no energy can be associated with gradients l outside the range $\pm 1/L$. Within this range the power distribution can be expressed exactly by a Fourier series

$$E(l) = \sum_{n=-\infty}^{\infty} A_n e^{i2\pi l n D} \text{ where } A_{-n} = A_n^*, D \leq \frac{1}{2}L$$

Suppose the gain curve is a finite series with the same arguments,

$$g(l) = \sum_{n=-N}^{n=N} B_n e^{i2\pi l n D}$$

Then from equation (11) the power output is also a finite series,

$$P(l_0) = \sum_{n=-N}^{n=N} A_n B_n e^{i2\pi l_0 n D}$$

By a well-known property of the Fourier series (see for instance Churchill, 1941) the mean square difference between $P(l_0)$ and $E(l_0)$ is a minimum if the coefficients $A_n B_n$ are equal to the coefficients A_n of the Fourier series, that is, if the B_n are all unity. Arsac's conclusion is that the most desirable array is one whose gain curve has the form

$$\begin{aligned} g(l) &= \sum_{n=-N}^{n=N} e^{i2\pi l n D} \\ &= 1 + 2 \sum_{n=1}^{n=N} \cos 2\pi l n D \\ &= \frac{\sin \pi l D (2N + 1)}{\sin \pi l D} \end{aligned} \quad \dots\dots\dots (12)$$

He points out that because this curve takes many negative values an array with this gain curve cannot be realised, but draws attention to examples of arrays with three and four receivers whose gain curves differ from this "optimum" form only by an additive constant. The array pictured in Fig. 2 is an example. The receivers all have unit sensitivity and the coefficients in the gain curve are all unity except B_0 which is 3. This means that the output power $P(l_0)$ differs from the "optimum" by a constant term $2A_0$. In practice it would be easy to use the array to find a curve of power and then to shift the zero by subtracting a suitable constant, actually twice the power output of a single receiver. In effect this shifts the zero of the gain curve and it takes the "optimum" form shown by the broken line in Fig. 2 (c). Arsac has made and used a set of four receivers set at positions O, D, 4D, and 6D. This array can be brought to its "optimum" form in a similar way.

Arsac goes on to discuss possible arrangements of more than four receivers but points out that they cannot be brought to an "optimum" arrangement by subtracting a constant power. He gives many examples of approximations to the "optimum" form. They all show great economy in the number of receivers in comparison with arrays where receivers are set at a uniform spacing, but they all show unpleasant features merely because they do not achieve the "optimum" form. Curve A of Fig. 5 is an example.

In subsequent sections it will be shown how it is possible to create extensive line-arrays that have "optimum" gain curves. Figure 5 will serve as the first example. If the set of six receivers is used in the manner suggested by Arsac, their gain curve is curve A. If they are used in a different way their gain curve takes the "optimum" form shown as B, and the improvement is obvious.

It is of interest to note that a system which possesses an optimum gain curve in two dimensions is already well known. This is the Mills cross. Its behaviour is discussed in the next section.

THE MILLS CROSS

The Mills cross (Mills and Little, 1953) uses two sets of similar antennae set in lines at right angles in the manner of Fig. 3 (a). Actually the cross described by Mills and Little used 12 antennae in each of the four arms and the central receiver was omitted. Fig. 3 (op. cit.) will serve, however, for discussion.

The quantity that is measured is in effect the mean product of the total signals from the two sets of receivers. Let there be N receivers separated by intervals D in each of the four arms. Writing $u_{-N}, \dots, u_N$ and $v_{-N}, \dots, v_N$ for the individual signals, their totals are

$$U(t) = \sum_{r=-N}^{r=N} u_r(t) \quad V(t) = \sum_{s=-N}^{s=N} v_s(t)$$

The quantity that is measured is

$$\text{Power} = \overline{U \cdot V} = \sum_{r=-N}^{r=N} \sum_{s=-N}^{s=N} \overline{u_r \cdot v_s} \quad \dots\dots\dots (13)$$

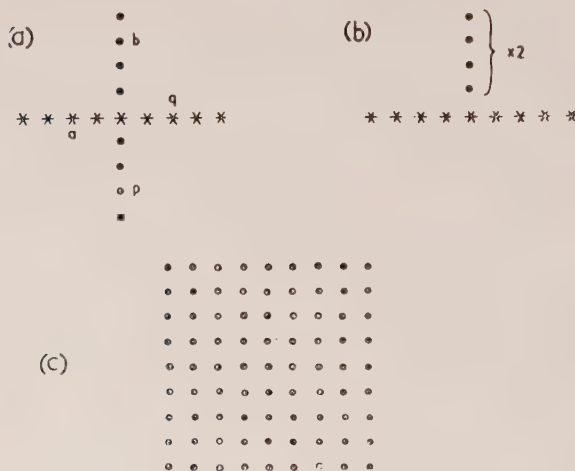


FIG. 3.—The two sets of antennæ in the Mills cross (a) are indicated by dots and asterisks. The central receiver is a member of both sets. The set of space intervals implicit in the power output of the Mills cross is the uniform square set shown in (c). This set is the spectrum of its two-dimensioned gain function which in consequence is an optimum one. One arm of the cross can be omitted as in (b) without changing its gain function, so long as the signals from the opposite arm are doubled in amplitude.

Each of the mean products in this summation is a value of the space correlogram for a certain space interval, the value being weighted by the sensitivities of the receivers. It can readily be seen that the plot of all these space intervals is the complete square set that is pictured in Fig. 3 (c). This set of points, weighted by the sensitivity factors, is the spectrum of the power gain function of the Mills Cross. Because each point is represented once and only once and because the sensitivity factors are all equal, the Mills cross has in two dimensions an "optimum" gain function. Thus, a typical product in equation (13) is, by an obvious extension to two dimensions,

$$\overline{u_r \cdot v_s} = \rho(rD, -sD) = \int_{-\infty}^{l=\infty} \int_{-\infty}^{m=\infty} E(l, m) \cdot \cos 2\pi(lr - ms)D \cdot dl dm$$

The gain function is therefore

$$g(l, m) = \sum_{r=-N}^{r=N} \sum_{s=-N}^{s=N} \cos 2\pi(lr - ms)D \quad \dots\dots\dots (14)$$

This point of view also shows that some of the receivers in the cross are unnecessary. The pair of antennae marked "a" and "b" in Fig. 3 (a) present the same space interval as the pair marked "p" and "q". In Fig. 3 (c) these were represented by diametrically opposite points, but this formal change of sign in the interval makes no difference in the mean products of the signals. In short, one arm of the Mills cross can be omitted entirely and the gain function will be unchanged, provided the signals from the opposite arm are doubled in amplitude. Fig. 3 (b) shows this equivalent form of the Mills cross. The gain function is

$$\begin{aligned} g(l, m) &= \sum_{r=-N}^{r=N} \left(\cos 2\pi lrD + 2 \sum_{s=1}^{s=N} \cos 2\pi(lr - ms)D \right) \\ &= \sum_{r=-N}^{r=N} \sum_{s=-N}^{s=N} \cos 2\pi(lr - ms)D \end{aligned}$$

as before.

A LINE-ARRAY OF SIX RECEIVERS

If the power outputs of different arrays are subtracted, then in effect their gain curves are subtracted. Equation (11) leads to the result

$$P_1(l_0) - P_2(l_0) = \int_{-\infty}^{\infty} E(l) \cdot [g_1(l - l_0) - g_2(l - l_0)] dl \quad \dots\dots\dots (15)$$

By combining outputs in this way it is possible to produce an output which has a gain curve of the optimum form.

In the example of Fig. 2 and in the arrangement of four receivers used by Arsac, the gain g_2 and the output P_2 were constants. A more complicated example is illustrated in Fig. 4. Six receivers of equal sensitivity occupy positions O, D, 4D, 7D, 10D, and 12D (Fig. 4, a). Arsac has quoted this as a possible array and has calculated the gain curve shown as A in Fig. 5. The convolution of the array is shown in Fig. 4 (b). Because some of the intervals appear more than once, and so have more than unit weighting the arrangement is not an opti-

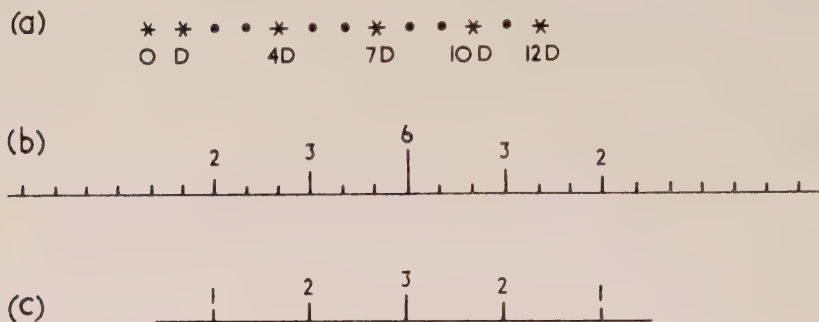


FIG. 4.—A set of six receivers at positions O, D, 4D, 7D, 10D, 12D is indicated by the asterisks in (a). Its convolution is shown in (b). Its supernumerary terms are present in (c) which is the convolution of the sub-array formed by receivers at positions 4D, 7D, and 10D.

imum one and curve A of Fig. 5 shows an undesirable large gain near $2\pi/3$. Consider, however, the receivers that occupy positions 4D, 7D, and 10D. If these three are treated as an array, they have the convolution shown in Fig. 4 (c). This presents nearly all the supernumerary intervals that occur in (b). Further, the convolution of a single receiver acting alone is a single zero interval. It can readily be seen that if outputs are found simultaneously from the whole array, P , from the set of three receivers, P_3 , and from any single receiver in the system, P_1 , the combination

$$P - P_3 - 2P_1$$

is an output which has an optimum gain curve; the convolutions combine to give a set of intervals all with unit weighting. The gain curve is then

$$g(l) = 1 + 2 \sum_{n=1}^{n=12} \cos 2\pi n l D$$

and is shown as curve B in Fig. 5.

There is some loss of power when an optimum gain curve is produced in this way. The two gain curves in Fig. 5 have been scaled to the same maximum to aid comparison, but curve A should have a peak value of 36 since it comes from 6 receivers. The gain curve B should have a peak of

$$6^2 = 3^2 = 2$$

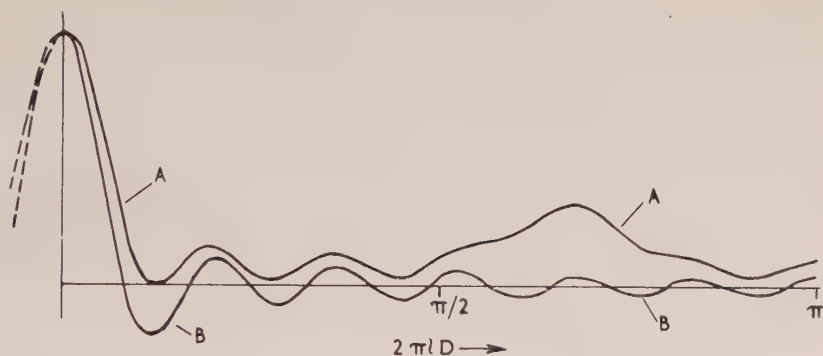


FIG. 5.—Curve A is the gain curve of the original array in Fig. 4 (a). Curve B is an "optimum" gain curve. It is got by subtracting from the power output of the array, the power output of the sub-array and twice the power output of a single receiver. Optimum output $= P - P_s - 2P_1$.

or 25. This difference in sensitivity is not so great as to offset the improved form of the curve.

OTHER LINE-ARRAYS

The same method can produce "optimum" outputs from larger arrays. The following table shows six, seven, and eight receivers arranged according to three different systems. The systems are devised so that the various pairs of receivers present every interval D , $2D$, $3D$ ND , where ND is the overall length.

TABLE I—Some "Optimum" Line-Arrays

System	6 receivers						7 receivers						8 receivers								
"3"	1	3	(3	3)	2	[12]	1	3	(3	3	3)	2	[15]	1	3	(3	3	3)	2	[18]	
"4"	1	(1)	4	(4)	3	[13]	1	(1)	4	(4	4)	3	[17]	1	(1)	4	(4	4	4)	3	[21]
"5"	1	(1	1)	5	4	[12]	1	(1	1)	5	(5)	4	[17]	1	(1	1)	5	(5	5)	4	[22]

The numbers in square brackets show the total length of the array in multiples of a unit distance D . The preceding sets of figures are the intervals between successive receivers in the array, expressed as multiples of D . Those intervals included in parentheses show the sub-array or sub-arrays whose power must be subtracted from the power of the whole array in order to produce an output with an optimum gain curve. Strictly speaking it is necessary to subtract also the power output of a single receiver, but since this only contributes a constant term

to the output, its omission from the table is not of major importance. It must be subtracted twice in a "3" system and once in a "4" or higher system.

A "3" system using six receivers has already been illustrated in Fig. 5. More receivers can be used merely by using more intervals of length 3 units in the middle of the array. With seven or eight receivers, however, a "4" system or a "5" system can lead to a longer array and consequently to a higher resolving power.

In a " n " system the central intervals of the array are n units long. The last interval is $(n - 1)$ units long and the first $(n - 2)$ intervals are all one unit long. Then if K receivers are used the whole array has an overall length of N units where

$$N = n(K + 2 - n) - 3 \quad \dots\dots\dots (16)$$

The maximum overall length, and consequently the maximum resolving power, is given by a system in which n is $(h + 1)$ where K is either $2h$ or $2h + 1$. For such arrangements

$$N = \frac{1}{4}K^2 + K - 2 \quad , \quad K \text{ even}$$

$$N = \frac{1}{4}K^2 + K - 2\frac{1}{4} \quad , \quad K \text{ odd}$$

Some numerical values for these best arrangements are shown in Table 2.

TABLE 2—Optimum Line-Arrays

$K = 6$	7	8	9	10	11	12	13	14	15	16
$N = 13$	17	22	27	33	39	46	53	61	69	78
$n = 4$	(4, 5)	5	(5, 6)	6	(6, 7)	7	(7, 8)	8	(8, 9)	9

The table shows the overall length, N units, of an array of K receivers when they are arranged to best advantage in an " n " system.

As an illustration, Fig. 6 shows a set of 10 receivers arranged in a "6" system which gives the array an overall length of 33 units. Curve (a) shows the gain curve of this array.

OPTIMUM ARRAYS FOR THE STUDY OF POINT SOURCES

The gain curves of "optimum" arrays possess many side lobes. The curves in Fig. 5 (b) and Fig. 6 (a) are examples. These side lobes make the arrays unsuitable as they stand for detecting and resolving point-sources. Fig. 7 (a) illustrates the difficulty. This curve shows

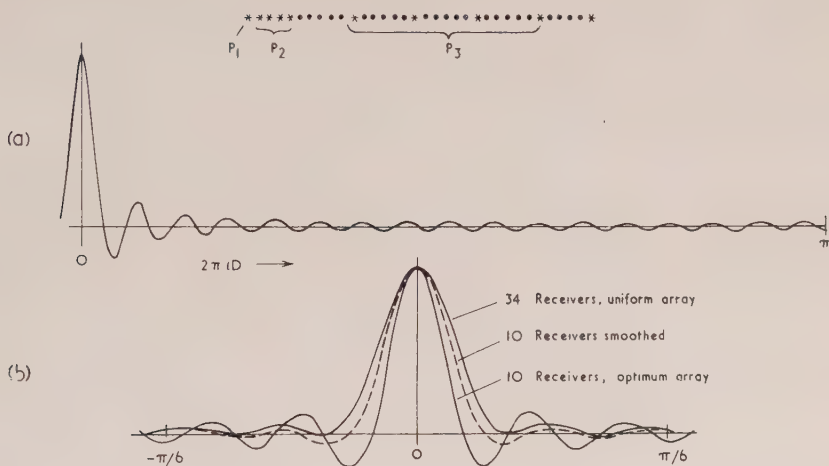


FIG. 6.—Ten receivers in a "6" system cover a length of 33 units. The combination of power outputs ($P - P_3 - P_2 - P_1$) has the optimum gain curve shown in (a). The mid portion of the gain curve is compared in (b) with the gain curve of the 10 receivers when the output is smoothed, and with the gain curve of a uniform array having the same overall length and using 34 receivers.

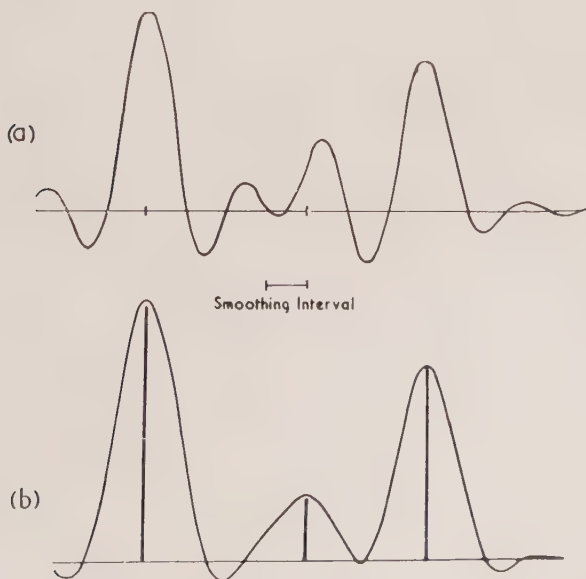


FIG. 7.—Curve (a) shows how three power sources would be represented by an "optimum" array. Curve (b) is obtained by smoothing curve (a) and the third, minor, source is then evident.

how the "optimum" array pictured in Fig. 7 would represent three point-sources which were unequal in strength and fairly close together. The curve is the sum of three curves similar to 6 (a). The experimenter must judge the position and strength of the three point-sources by picking out the positions and heights of the three main peaks. Two of these main peaks are obvious, but the third is obscured by the side lobes of the other, stronger ones.

Nevertheless, the "optimum" systems are very economical in receivers and it should be asked whether one might not so modify an "optimum" system that the side lobes were attenuated. Mills has done this. His crossed lines of receivers (Fig. 3) would be an "optimum" system if the receivers were all of equal sensitivity. By weighting them appropriately the side lobes are made sufficiently small for the cross to be used to resolve radio "stars".

The same technique cannot be used with the line-arrays summarised in Table 2. However, there are other ways. The subsidiary maxima in the measured curve of power are narrower than the main peaks and if the measured curve is smoothed by any convenient process the subsidiary maxima can be attenuated relatively to the main peaks. For instance, curve 7 (b) has been got from curve 7 (a) by plotting the sum of pairs of ordinates separated in 7 (a) by the fixed interval shown on the diagram. The interval is that between successive maxima and minima in the gain curve of the array. In curve 7 (b) the peaks representing all three point sources are quite obvious. The upright lines on 7 (b) mark the positions and relative strengths of the three sources which were used in constructing curve 7 (a). Evidently the peaks in curve 7 (b) indicate these sources quite well.

The improvements can be thought of as arising from a change in the form of the gain curve. The smoothing process modifies the gain curve in the same way as it modifies the power curve to which it is applied. Fig. 6 (b) shows the central portion of the optimum gain curve in 6 (a) and also shows as a broken line the gain curve that is produced by the smoothing process illustrated in Fig. 7. For comparison the gain curve of a uniform array of equal length is shown as well. For the purpose of resolving point sources there seems little to choose between the smoothed output power of 10 receivers in an optimum array and the output power of 34 receivers used in a uniform array.

The curves of Fig. 6 (b) are in fact plotted from approximate formulae for arrays of length N units.

$$\text{Optimum array } g(l) = \sin x/x$$

$$\text{Smoothed optimum array } g(l) = \cos x/[1 - 4(x/\pi)^2]$$

$$\text{Uniform array } g(l) = [\sin \frac{1}{2}x/\frac{1}{2}x]^2$$

$$\text{where } x = (2N + 1)\pi l/D$$

These are close approximations to the central parts of the gain curves so long as N is large. Fig. 6 (b) indicates that the smoothed output of

an optimum array using K receivers is as suitable for resolving point sources as is the output of a uniform array using $N + 1$ receivers where some typical values of N_i and K have been listed in Table 2.

The smoothing process illustrated in Fig. 7 could be obtained without computation by processing the signals from the receivers in two separate channels so as to get two "optimum" outputs corresponding to two values of l_0 differing by $1/(2N + 1)D$. The sum of these two outputs is the "smoothed" output.

CONCLUSIONS

Arrays that have gain curves of the "optimum" form can be realised in practice. The Mills cross is an example of such an array working in two dimensions. Methods have been shown for getting an "optimum" gain curve from line-arrays.

The "optimum" arrangement leads not only to a more accurate measure of any distributed source of power, but it leads also to a great reduction in the number of receivers that are needed.

For the purpose of detecting and resolving point sources, methods have been described for attenuating the side lobes without using more receivers.

ACKNOWLEDGEMENTS

The writer wishes to thank his colleagues, in particular Messrs J. E. Drummond and K. I. Williamson, for suggesting a number of modifications in the text.

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CORROSION OF MILD STEEL IN SOME NEW ZEALAND SOILS

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(Received for publication, 16 October 1957)

Summary

Mild steel plates were buried horizontally at a depth of 3 ft at 23 sites in New Zealand soils. After $2\frac{1}{2}$ years' burial the plates were cleaned, weighed, pit depths measured, and corrosion described. Samples of soil in which the plates were buried were analysed and field conditions were noted. The results have been examined statistically and an attempt made to correlate corrosion with soil analyses and field conditions. The most highly corrosive soils were clays of a high total acidity that were subject to alternate wetting and drying. Considerable attack occurred in soils high in soluble salts. Slight to moderate even attack without much pitting was confined to waterlogged soils.

INTRODUCTION

Gemmell (1952) recorded the corrosion resulting from 12 to 13 years' burial of bare mild steel in soils. These plates had been laid down by the New Zealand Institution of Engineers in 1934¹. The tests confirmed the results of earlier work overseas (e.g. Logan, 1945, pp. 216-29) that high or low corrosiveness of a soil can usually be detected by an extreme value of one or more of the corrosive factors. Where the soil properties have intermediate values prediction of corrosion is much less reliable.

Soil factors favourable to corrosion include:

Differential Aeration

This may be caused by uneven contact between the metal and soil. It may also occur between the upper and lower surfaces of buried plates or pipes, especially if these have been buried in the zone of fluctuation of the water-table.

Low Electrical Resistance

Corrosion is always accompanied by a flow of electrical current and hence a soil of low resistance causes greater attack on the metal. In soils a low resistance usually indicates high salt concentration.

High Total Acidity

Total acidity is the titratable acidity or exchangeable hydrogen in a soil, as distinct from the pH. Because the acids in a soil are only slightly dissociated, the pH value may not be a measure of the corrosiveness of a soil.

High Moisture-Holding Capacity

This is a property associated with clays and peats. It enables corrosion to continue for long periods after rain.

Sulphate-Reducing Bacteria

These are anaerobic. In addition to absence of oxygen they require a favourable pH (5.5 to 8.5, maximum activity near neutral) and organic matter, as well as sulphates or other reducible sulphur compounds. These bacteria utilise the cathodic hydrogen produced by solution of iron. Polarization is prevented and corrosion continues without drop in rate.

Other Factors

A single soil property may favour corrosion in several ways. For instance, an acid clay will have a high total acidity, high moisture-holding capacity, and may cause high differential aeration. Because inter-relationships are not fully understood prediction of corrosion from soil properties is unreliable.

Along pipelines other factors such as differences of soil type, presence of cinders or other foreign material in the backfill, and stray-current electrolysis are also important, but do not apply to these field tests which were carried out with small samples in undisturbed soils.

The earlier test sites (Gemmell 1952) were all in towns and included only a restricted range of soils. The present tests extend the field work to cover the principal soils of New Zealand. It is planned to continue these tests for at least 10 years. Although later inspections may modify the conclusions, it was considered useful to record in this paper the results of burial for $2\frac{1}{2}$ years.

EXPERIMENTAL

The twenty-three sites chosen in both the North and South Islands include the main soils in the genetic classification of New Zealand soils (Taylor, 1948).

Mild steel* plates 15 in. x $9\frac{1}{2}$ in. x $\frac{3}{16}$ in. (approx.) with a surface

*Analysis of a plate by the Dominion Laboratory gave the following results:

	%		%
C	0.25	Mo	0.01
P	0.32	Cu	0.04
S	0.038	W and Zr	0.05
Si	0.06	Ti, Co, Sn, and Pb	0.02
Mn	0.44	Va	0.01
Ni	0.02	Al	0.005

The carbon, phosphorus, and sulphur were determined chemically, and the remaining elements estimated by spectrographic means.

area of 2.06 sq. ft (19.2 sq. dm.) were used in the tests. The samples were cut from one batch of plate although it is known that soil differences have greater effect than variations in the steel (e.g. Hudson and Acock, 1952). Scale was removed from the plates by pickling in hot 10% ammonium citrate solution made alkaline with ammonia. Each plate was weighed before burial and the average weight was 3,400 g.

At each site five pits 3 ft square and 3 ft deep were dug and, in each pit, four plates were buried horizontally, one at each corner. Pits were separated by 2 ft, so that removal of samples from one pit would have little if any effect on the others, particularly as regards drainage.

Two plates from each site were dug up (1953-4) after $2\frac{1}{2}$ years' burial and were again cleaned in hot 10% ammonium citrate solution containing excess ammonia. This removes the rust but has a negligible effect on the uncorroded steel (Logan, 1945, p. 302). The plates were brushed occasionally with a stiff bristle brush to hasten the process and stubborn rust at the bottom of pits in the plates was loosened with a sharp point. After cleaning, the plates were rinsed in running water and dried with a cotton cloth.

LABORATORY TESTS

The results of the tests on plates are recorded in Table 2 and soil data are listed in Table 3.

Terms Used in Table 2 (Plate Data)

Average Penetration—After cleaning, the plates were weighed and the average penetration calculated from the equation

$$\text{average penetration} = \frac{\text{loss of weight}}{\text{density of material} \times \text{area of plate}}$$

Pit-Depths—Maximum pit-depths were measured with a dial gauge equipped with a slender probe (Gemmell, 1952). The original surface of many of the plates had been destroyed in the ground, and the resulting irregularities precluded accurate measurements. The results are therefore slightly low.

Pitting factor is the ratio of the maximum pit-depth to the average penetration, the higher the value the greater the tendency for attack to take the form of pitting rather than of general corrosion. The pitting factor has been calculated from the average of the maximum pit-depths on the top and bottom surfaces.

Description of Attack—The method used is essentially that given by Champion (1952), but instead of code numbers approximate values for the distribution and depth of attack are used. The corrosion observed has been classified in three main categories; general, semi-local,

and pitting. These are further subdivided as shown in Table 1. General corrosion is defined as attack to an approximately uniform depth over the whole surface. Semi-local corrosion is similar but is confined to restricted areas which are large compared with the depth of attack. While the attack remains of these two types the metal is not likely to fail from perforation. The term pitting is used when the attack is so localised that the width is of the same order as the depth of attack. The danger of failure by perforation is then high and the depth of attack is of major importance.

TABLE 1 (Champion, 1952).—Classification of Corrosion and Abbreviations used in Table 2.

				average width/depth ratio					abbreviation
General corrosion									
even					—				Ge
uneven					—				Gu
Semi-local corrosion									
even	}				20				Le
uneven									
Pitting									
wide					4				W
medium					1				M
narrow					$\frac{1}{4}$				N

In Table 2 the abbreviation for the type of attack in each instance is supplemented by figures for the number of affected areas and the depth of attack. Corrosion in soils is commonly uneven, both the type and intensity of attack varying over a few inches. Each type of attack is therefore described separately and the area affected by each type is given as a percentage. Because of the unevenness of attack the figures given for the average number, size, and depth of pits are only approximate. Where the variation has been very great the range is given. The appearance of the plates is often distinctive and the boundaries of the pits are described in the tables as rounded, sharp, or undercut.

Terms Used in Table 3 (Soil Data)

Field moisture is the amount of water expressed as a percentage of the soil after drying at 105°C. This value is relevant, as soil corrosion is an electrolytic process and will not proceed in the absence of water.

TABLE 2.—Corrosion of Mild Steel Plates Buried in Soil for 2½ Years.
(Average of Two Plates)

Soil type (in order of decreasing corrosiveness)	Loss in weight (g)	Average penetra- tion (a) (mm)	Max. pit depth (b) top* and bottom† (mm)	Pitting factor (b)/(a)	Type of attack
Wairama clay loam	318	0·21	1·2* 1·4†	6	W Lu
Waitakere clay	265	0·18	1·6* 1·6†	9	M W Gu
Waiotira clay loam	262	0·18	1·5* 1·7†	9	W W W Lu Gu
(Blackmans)§ sandy loam	245	0·16	1·7* 1·4†	9	M-Lu M-Lu
Timaru silt loam	220	0·15	1·3* 1·7†	10	W Lu Lu
Ruatangata friable clay	185	0·12	1·2* 1·7†	11	M W W W
Rosedale silt loam	166	0·11	1·1* 1·2†	10	W W W
Wharekohe silt loam	153	0·10	0·7* 0·8†	7	W W
New Plymouth black loam	132	0·09	1·2* 1·0†	12	W W W W
Patua sandy loam	116	0·08	0·4* 0·9†	8	Gu Lu
Matapiro sandy loam	99	0·07	0·37* 0·76†	8	M M
Motukarara sandy loam	93	0·06	0·3* 0·5†	6	Gu Gu
Foxton black sand	80	0·05	0·4* 0·5†	8·4	W M Lu

TABLE 2.—Corrosion of Mild Steel Plates Buried in Soil for 2½ Years.
(Average of Two Plates)

No. of pits per sq.dm.	Description of attack		% Total area affected	Remarks
	Width of pit (cm)	Depth of attack (mm)		
1,000	0.3	0.9	100	rounded edges
300	0.2-0.9	0.2-0.5	50	
600	0.15	0.4 }	100	rounded edges
20	0.6	1.0 }		
—	—	0.7 }	10	
15	0.4	0.8 }	100	rounded edges sloping sides
1,000	0.1	0.3 }		
500	0.2	0.5 }	25	
5	1.5	1.5 }		
—	—	0.1 }	75	
300	0.2-1.5	1	100	edges undercut
20	0.2-3	1	50	
100	0.2	0.8 }	100	sharp edges steep sides
10	1.5	0.3 }		
10	3	0.9 }	25	
1,000	0.2	0.5 }	100	steep edges
10	0.7	0.9 }		
10	1.0	1.1 }	25	
1,000	0.1	0.2 }	75	
10	0.6	0.8 }	100	
2,000	0.1	0.1 }		sharp edges
20	0.6	0.9 }	100	
300	0.1	0.6	100	rounded edges sloping sides
300	0.2	0.6	70	
5	0.4	0.9 }	100	rounded edges
1,000	0.06	0.25 }		
5	0.4	0.9 }	100	
300	0.1	0.2 }		
—	—	0.06	100	
5	3	0.2	100	
3,000	0.05	0.1	100	
3,000	0.1	0.3	100	
—	—	0.06	100	
—	—	0.07	50	
2,000	0.1	0.1	100	local attack has occurred where poor contact with soil
2,000	0.2	0.1 }	50	
10	0.3	0.04 }		

TABLE 2.—*Continued.*

Soil type (in order of decreasing corrosiveness)	Loss in weight (g)	Average penetra- tion (a) (mm)	Max. pit depth (b) top* and bottom† (mm)	Pitting factor (b)/(a)	Type of attack
Taupo (brown sand)§	68	0.05	0.98* 0.54†	15	Lu W Lu W
Rukuhia peat	65	0.04	0.2* 0.2†	5	Gu Gu
Kaiapo silt loam	55	0.04	0.29* 0.36†	8	Gu Gu W
Waipori silt loam	51	0.035	0.8* 0.7†	21	Gu W-Lu W
(Omarāma)§ fine sandy loam	35	0.02	0.45* 0.3†	20	Lu W Gu
Temuka silt loam	31.5	0.02	0.12* 0.15†	7	Gu Gu
Oamaru clay loam	27.5	0.02	0.7* 0.85†	39	W Lu Gu
Kaingaroa silty sand	26.5	0.02	0.47* 0.83†	31	Gu Lu Gu M
Okarito fine sandy loam	22	0.015	0.1* 0.15†	8	Ge Ge
Waimumu silt loam	16	0.01	0.2* 0.2†	20	Gu Gu

§Names in parentheses are provisional

TABLE 2.—*Continued.*

No. of pits per sq.dm.	Description of attack		% Total area affected	Remarks
	Width of pit (cm)	Depth of attack (mm)		
200	0.4	0.13 }	100	steep edged pits have occurred where pumice gravel has been cemented to surface
100	0.3	0.6 }		
100	1.5	0.05 }	100	
300	0.1	0.4 }		
—	—	0.04	100	
—	—	0.04	100	
—	—	0.03	100	
—	—	0.03 }	100	
3,000	0.06	0.1 }		steep sided pits
—	—	0.04 }	100	
200	0.1-0.3	0.1-0.4 }		
300	0.3	0.5	100	sharp edged pits often under- cut
300	0.1-0.3	0.02 }	100	steep edged pits
10	0.06	0.2 }		
—	—	0.02	100	
—	—	0.02	100	
50	0.1	0.3	100	
5	0.1-2	0.5	10	sharp edges, steep sides
—	—	0.02	90	
—	—	0.02 }	100	
200	1.0	0.1 }		
—	—	0.02 }	100	steep edged pits
5	0.13	0.5 }		
—	—	0.02	100	
—	—	0.02	100	
—	—	0.01	100	
—	—	0.01	100	

§Names in parentheses are provisional

TABLE 3.—Soil Data.

Soil type (in order of decreasing corrosiveness)	Soil classification	Locality and grid reference	Field texture at 3 ft	Topog- raphy
Wairama clay loam	yellow-brown earth, mod. weathered, mod. leached	Raglan N64 501479	Clay	Rolling
Waitakere clay	brown, granular clay, strongly leached	Waitakeres N42 151493	Clay	Rolling
Waiotira clay loam	yellow-brown earth, strongly weathered, mod. leached	Weki Valley N23 622863	Clay	Rolling
(Blackmans)* sandy loam	solonetz, weakly leached	Alexandra	Silt loam	Flat
Timaru silt loam	yellow-grey earth, mod. weathered, mod. leached	Timaru S111 792494	Fine sand	Flat
Ruatangata friable clay	red and brown loams, strongly leached	Ruatangata West N20 686048	Clay	Flat
Rosedale silt loam	yellow-brown earth, mod. weathered, mod. leached	Nelson S20 358177	Stony clay loam	Flat
Wharekohe silt loam	podzol, strongly weathered	Whangarei N19 617934	Clay	Flat
New Plymouth black loam	yellow-brown loam, mod. leached	Omata N108 579871	Sandy loam	Flat
Patua sandy loam	yellow-brown loam, strongly leached	Lower slopes, Mt. Egmont N108 610764	Sand	Rolling
Matapiro sandy loam	yellow-grey earth, mod. gammate, weakly leached	Havelock North N134 285161	Sandy clay loam	Flattish
Motukarara sandy loam	saline gley soil	Motukarara S84 941317	Sand	Flat
Foxton black sand	yellow-brown sand	Paraparaumu N157 546698	Sand	Flat

TABLE 3.—Soil Data.

Drainage	Annual rain- fall (in.)	Field mois- ture (% of dry wt.)	Centri- fuge moist. equiv. (% of dry wt.)	Resistivity (ohm cm $\times 10^{-3}$)		pH		Total acidity (me/100 cu.cm.)
				Field (in.) 0-18 0-36 0-72	Lab. (in.) 36	Field	Lab.	
Moderate	50	50.5	41	8.0 7.4 6.3	3.6	4.5	4.4	60
Moderate	70	71.6	42	15.0 15.0 13.0	5.0	4.6	4.4	70
Rapid	50	41.1	33	10.5 11.3 10.2	8.4	—	4.8	41.8
Slow	13	16.5	21	3.1 4.2 8.4	1.7	—	9.1	0
Rapid	25		19	5.5 2.5 1.5	1.1	—	6.8	7.0
Moderate	60	40.4	37	6.5 11.2 19.7	7.5	4.7	5.2	20.4
Moderate	45	24.1	25	61.7 77.5 130	26	4.9	5.2	26
Slow, perched water table	50	28.8	23	14.3 17.8 14.7	8	—	4.6	17.1
Rapid	60	87.6	24	32.5 20 12	4.7	—	6.0	41
Rapid	90	120	28	94 87 115	15.5	5.4	5.7	56
Slow, perched water table	30	34.1	35	8.0 5.0 3.0	2.1	5.0	5.9	16.4
Moderate	25	25.6	3	25.0 20.0 10.0	9.8	6.5	7.4	0.8
Rapid	40	7.9	4	129 132 138	9.7	7.0	6.6	5.2

TABLE 3.—*Continued.*

Soil type (in order of decreasing corrosiveness)	Soil classification	Locality and grid reference	Field texture at 3 ft	Topog- raphy
Taupo (brown sand)*	yellow-brown pumice soil, mod. leached	Wairakei N94/4 598485	Pumice gravel	Rolling
Rukuhia peat	organic soil (acid peat)	Rukuhia N65 785375	Peat	Flat
Kaiapo silt loam	gleyed recent soil	Hastings N134 235218	Silt loam	Flat
Waipori silt loam	yellow-brown earth, weakly weathered	Waipori S163 670782	Silt loam	Rolling
(Omarama)* fine sandy loam	brown-grey earth, moderately leached	Lower Shotover	Gravel	Flat
Temuka silt loam	gley soil	Hinds S103 173980	Sand	Flat
Oamaru clay loam	rendzina	Oamaru S136 482627	Clay loam	Flat
Kaingaroa silty sand	yellow-brown pumice soil, strongly leached	Waimihia N103 740230	Coarse sand	Flattish
Okarito fine sandy loam	gley podzol	Greymouth S44 792889	Fine sandy loam	Flat
Waimumu silt loam	yellow-brown earth, weakly gannate, mod. leached, mod. gleyed	Gore S170 770397	Silty clay loam	Flat

*Names in parentheses are provisional.

TABLE 3.—*Continued.*

Drainage	Annual rain- fall (in.)	Field mois- ture (% of dry wt.)	Centri- fuge moist. equiv. (% of dry wt.)	Resistivity (ohm cm $\times 10^{-3}$)		pH		Total acidity (me/100 cu.cm.)
				Field (in.) 0-18 0-36 0-72	Lab. (in.) 36	Field	Lab.	
Rapid	45	39.6	11	287 465 800	10.8	6.6	5.9	6.0
Extremely slow	45	666	—	9.5 10.0 13.5	5.0	3.4	3.6	43
Slow, perched water table	32	61.7	44	2.0 2.3 2.5	3.6	—	6.6	10.0
Moderate	40	16.5	15	220 330 440	11.4	—	4.9	19.0
Rapid	30	1.1	16	270 480 840	23.6	—	5.7	10.6
Slow	30	22.6	15	7.4 10.0 14.0	16.0	6.3	6.4	3.7
Moderate	20	32.1	60	3.05 3.4 4.6	7.1	—	6.7	54
Rapid	58	39.8	14	580 810 870	4.3	—	6.4	2.4
Slow	100	—	26	41.6 57.0 111	24.8	—	5.2	28
Slow	35	25.9	26	11.5 11.8 9.0	7.0	5.7	5.45	15.6

*Names in parentheses are provisional.

Values, on a dry weight basis, range from 1% in gravelly soils to 700% in peats.

Centrifuge moisture equivalent is the amount of moisture expressed as a percentage of the weight of the oven-dry soil retained by the soil which has been first saturated with water and then subjected to a force equal to 1,000 times the force of gravity for 1 hr. The centrifuge moisture equivalent was determined by the engineering method (American Society for Testing Materials, 1950). Values greater than 40% are very high. Centrifuge moisture equivalent usually correlates well with field moisture.

Resistivity measurements were determined in the laboratory on water-saturated samples at a uniform compaction. The conductivity cell used is described by Gemmell (1952). Values given by this method on New Zealand soils range from 300 ohm cm for a saline soil to 30,000 ohm cm in unweathered sands or gravels.

Resistivity measurements were determined in the field with a four-terminal megger. The method is described by Wenner (1916). Values of field resistivity were in general of the same order as those of laboratory resistivity but dry soils gave higher values in the field than in the laboratory. As only one field resistivity measurement at each site has been made, results must be considered as tentative. A number of measurements will be needed before a reliable average can be given.

pH was determined on $1/2\frac{1}{2}$ soil/water suspension with a glass electrode pH meter. The pH correlates well with other soil properties, e.g. saline soils usually have a high pH and acid peats and leached clay soils have low pH.

Total acidity. As the acids in soils are only slightly dissociated the pH value may not indicate the corrosiveness of a soil. The total quantity of ionisable hydrogen—the titratable acidity or exchangeable hydrogen—is a much better measure of its corrosiveness. The method used is essentially that due to Ewing (1934). Briefly, 5g of air-dried soil and 25 ml of normal sodium chloride solution are shaken together and titrated with 0.2N sodium carbonate solution to pH 8 using a glass electrode pH meter. Indicators are unsatisfactory because of their absorption by the clay. The figures have been recalculated to give the total acidity as milligramme equivalents (mge) per 100 cu. cm. of soil in the field condition. Usually the difference between this and the total acidity as mge per 100 g of air-dried soil is not large, as the dry bulk specific gravity of most soils is approximately 1 (range 0.5 to 1.5) but for peats the figure is 0.2 or less. For acid peats, values over 300 mge per 100 g are obtained on air-dried soils. This is reduced to 40 mge when recalculated as mge per 100 cu. cm. of soil at field density. Values up to 70 mge per 100 g air-dried soil (or 70 mge per 100 cu. cm. soil at field density) have been obtained for acid clays.

A statistical analysis has been carried out on some of the results shown in Table 2 and 3. Laboratory results were considered to be more reliable than field results in calculating a regression.

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_5 x_5 + b_6 x_6$$

where Y = loss in weight (g)

X_1 = total acidity (mge per 100 cu.cm)

X_2 = field moisture (%)

X_3 = laboratory pH

X_4 = laboratory resistivity ohm cm $\times 10^{-3}$

X_5 = centrifuge moisture equivalent (%)

X_6 = annual rainfall (in.)

The following values were obtained:

	Regression coefficient	Standard deviation
b_0	-286.39	
b_1 (total acidity)	1.792	0.635**
b_2 (field moisture)	2.255	3.917
b_3 (lab. pH)	63.070	34.451*
b_4 (lab. resistivity)	-1.256	2.223
b_5 (centrifuge moisture equivalent)	-2.872	10.897
b_6 (rainfall)	-0.2117	7.585

*Significant at the 5% level.

**Significant at the 1% level.

The analysis of variance for the regression using all six factors is given in Table 4 and, for total acidity and pH only, is shown in Table 5. The ratio of the sum of squares 124,070/179,664 in Table 4 shows that 70% of the variation in corrosion observed at the different sites can be accounted for by the six factors analysed. Table 5 shows that 50% of the variation is accounted for by the total acidity alone and 60% by total acidity and pH. Thus, the inclusion of the other four variables, field moisture, resistivity, centrifuge moisture equivalent, and rainfall, reduces the residual mean square from 3,805 to 3,474, a difference of only 331. This indicates that from the data analysed, there is little reason to suggest that these factors have a large effect on the corrosion. Although two-thirds of the variation can be explained by the six factors considered, the high remaining variation shows that the regression is of little use in predicting corrosion. The standard deviation with all six variables is almost 60, that is, approximately 67% of the observed losses in weight could be predicted with a possible accuracy of ± 60 g and 95% with an accuracy of ± 120 g. This is many times the minimum weight loss of 16 g and a large part of the maximum weight loss of 316 g.

Correlations between the six soil properties and loss in weight are given in Table 6. Total acidity gives the only significant correlation with weight loss and reinforces the conclusion that total acidity is the main corrosive factor. The correlations between the various soil properties are not unexpected. Clays and peats have a high total acidity and high-moisture-holding capacity as shown by the positive correlation, significant at the 1% level, with field moisture and with centri-

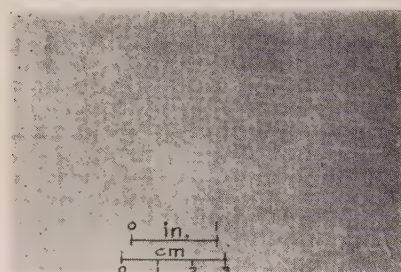


FIG. 1.—Uncorroded plate.

TABLE 4.—Analysis of Variance for the Six Variables.

	Sum of squares	Degrees of freedom	Mean square	F value
Variation attributable to linear regression	124,070	6	20,678	5.95**
Remainder	55,594	16	3,475	—
Totals	179,664	22	—	—

**Significant at the 1% level.

TABLE 5.—Analysis of Variance for Total Acidity and pH.

	Sum of squares	Degrees of freedom	Mean square
Variation explained by the total acidity	89,737	1	89,737
Increment explained by the pH	13,823	1	13,823
Residual	76,104	20	—
Totals	179,664	22	3,805

TABLE 6.—Correlations.

	Loss in weight	Total acidity	Field moisture	pH	Resistivity	Centrifuge moisture equivalent	Rainfall
Loss in wt.	1.000	0.5151	0.2453	-0.2747	-0.3542	0.3208	0.2856
Total acidity		1.0000	0.6275**	-0.2532	0.0927	0.7493**	0.5271*
Field moisture			1.0000	-0.3018	-0.2161	-0.3500	0.4125
pH				1.0000	-0.0234	0.2750	-0.5342**
Resistivity					1.0000	-0.3379	-0.4631*
Centrifuge moisture equivalent						1.0000	0.1151
Rainfall							1.0000

*Significant at the 5% level.

**Significant at the 1% level.

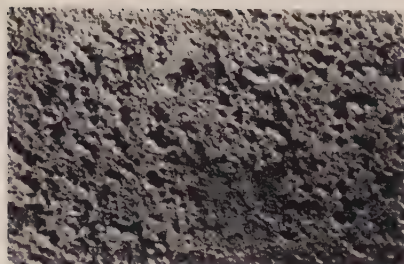


FIG. 2.—Upper surface of plate from Wairama clay loam.

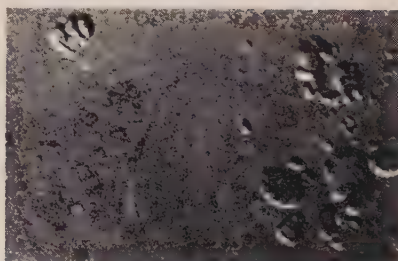


FIG. 3.—Lower surface of plate from Wairama clay loam.

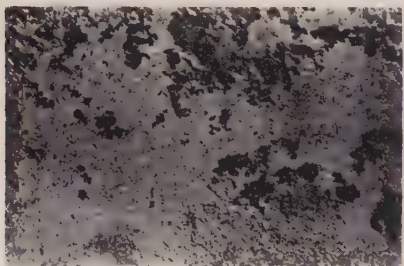


FIG. 4.—Upper surface of plate from Blackmans fine sandy loam.

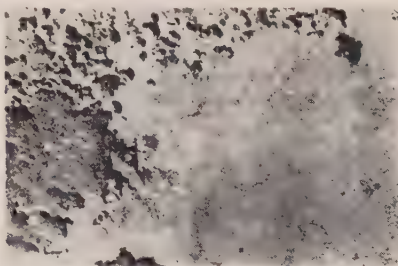


FIG. 5.—Lower surface of plate from Blackmans fine sandy loam.



FIG. 6.—Upper surface of plate from Rukuhia peat.

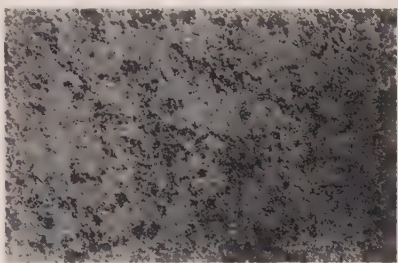


FIG. 7.—Upper surface of plate from Foxton black sand.

—Photos. R. R. Julian.

(Scale as for Fig. 1.)

fugé moisture equivalent. Strongly leached acid clays are more likely to occur in areas of high rainfall. The correlation between total acidity and rainfall is significant at the 5% level. As alkaline soils occur in low rainfall areas and highly leached acid soils occur only under high rainfall, values for rainfall correlate negatively with pH.

From the statistical analysis it is clear that it is not possible to predict soil corrosion with any accuracy from the laboratory soil tests made. This failure to get significant results from a consideration of

most of the "corrosive factors" is due to the comparatively small number of samples, and the large number of factors involved. If field conditions are considered the picture is clearer and the soils can be grouped according to the severity and type of attack.

The clay soils with moderate to rapid drainage and well developed structure are clearly the most corrosive: Wairama clay loam, Waitakere clay, and Waioitira clay loam. The corrosion in these soils is typically pitting, giving large deep pits with rounded edges and sloping sides (see Fig. 1, unused plate, and Fig. 2, upper surface of plate from Wairama clay loam). In Fig. 2 all the surface has been attacked, none of the original surface remains. Because of the granular structure of the soil, differential aeration would be expected and large deep pits have developed. With the average penetration ranging from 0.18 to 0.22 mm (0.007 to 0.009 in.) and maximum pit-depths of 1.3 to 1.9 mm (0.05 to 0.075 in.) this corrosion is classed as severe. On the lower surface (Fig. 3) contact with the soil has been poor and deep pits have also resulted. The pits occur where contact has been good. The areas of poor contact show slight even corrosion. This poor bedding down of plates and tendency for larger deeper pits to occur on the lower surface has been noted by other workers (Logan, 1945, p. 89; Hudson and Acock, 1952, p. 18).

The two soils high in soluble salts as shown by the low resistivity, (Blackmans)* sandy loam (Figs 4 and 5) and Timaru silt loam—also showed severe corrosion with an average penetration of 0.15 to 0.17 mm (0.006 to 0.007 in.) and maximum pit-depths of 1.2 to 2 mm (0.047 to 0.079 in.). The pits in plates from both these soils had sharp edges and steep sides (Figs 4 and 5) and, although not exclusive to saline soils, steep and sharp edges with a tendency to be undercut were particularly obvious. Much of the original surface remained between pits.

Even attack without much pitting is confined to the poorly drained soils, Waimumu silt loam, Okarito fine sandy loam (gley podzol), Temuka silt loam (gley soil), Kaiapo silt loam (gleyed recent soil), and Rukuhia peat (acid peat) (Fig. 6). The attack in these soils is slight, ranging from 0.01 to 0.04 mm (0.0004 to 0.0016 in.), average penetration and maximum pit-depths from 0.1 to 0.4 mm (0.004 to 0.016 in.). Attack has been almost identical on the upper and lower surfaces due to good bedding down of these plates and absence of differential aeration.

The plates from the rapidly draining sandy soils, Foxton black sand (Fig. 7), Kaingaroa silty sand, Taupo brown sand, and Omarama fine sandy loam, show many shallow pits. The attack in these soils is low to moderate, ranging from 0.02 to 0.5 mm (0.001 to 0.002 in) average attack with pit-depths ranging from 0.4 to 0.75 mm (0.015 to 0.03 in.).

*Provisional name.

CONCLUSIONS

The results from 2½ years' burial of bare mild steel plates in 23 soils show that corrosion cannot be accurately predicted from the chemical and physical properties of the soils. A statistical analysis showed that 70% of the variation in corrosion could be explained by the factors considered, and 50% was accounted for by total acidity alone. Prediction was improved by consideration of field conditions. The most corrosive soils were strongly leached acid clays with moderate to rapid drainage and nutty structure. These soils produce large deep rounded pits. Soils high in soluble salts were also highly corrosive, and their attack predominantly pitting, the pits having undercut sides. Mild even attack was confined to wet slowly draining soils. Attack was low in dry rapidly draining soils. The corrosion produced in these dry soils consisted of many shallow pits.

ACKNOWLEDGEMENT

This programme of field tests was designed and commenced by Dr G. D. Gemmell, formerly of the Soil Bureau. The statistical analysis was carried out by Mr W. B. Taylor of the Applied Mathematics Laboratory, Department of Scientific and Industrial Research, Wellington.

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LOW-TEMPERATURE ADSORPTION OF VARIOUS GASES BY SOILS

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(Received for publication, 8 November 1957)

Summary

The gases, argon, nitrous oxide, and *n*-butane have been compared as to their suitability for measuring the surface areas of soils, where these have moderate to high values. The arrangement and dimensions of an apparatus suitable for this purpose are given. The results show that argon from "Argon-Arc" welding cylinders appears to be a satisfactory substitute for nitrogen. Purified *n*-butane tends to give high results and is suitable for a rough estimate of surface only. Results with nitrous oxide are always higher than those given by argon, and the difference is greater the higher the organic carbon content of the soil. With increasing organic carbon content, a longer time is taken for equilibrium to be reached with this gas. Nevertheless, the adsorption is still considered to be largely physical in nature. With carbon dioxide, a similar—but smaller—effect is obtained. Surface areas of soils may be altered by chemical pretreatment and ageing of treated samples.

INTRODUCTION

For reliable measurements of the surface area of soils and soil colloids, the adsorption of nitrogen (Emmett *et al.*, 1938; Makower *et al.*, 1937), or argon (Emmett *et al.*, 1938), or ethane (Nelson and Hendricks, 1943) at temperatures near the boiling-points of these gases has been considered suitable. In the course of a series of measurements of surface areas of subsoils of volcanic origin, and of fine fractions extracted from them, the selection of suitable gases on the basis of ready availability and convenience of operation was investigated.

The principal gases used were nitrogen, argon, nitrous oxide, and *n*-butane. Commercial nitrogen usually requires purification to remove oxygen, and unless liquid nitrogen is available as a cooling bath, the alternative cooling medium of liquid oxygen restricts the range of partial pressures* with conventional apparatus. Argon is obtainable commercially in a high state of purity, and a liquid-oxygen bath enables a satisfactory range of partial pressure to be obtained. Nitrous oxide is obtainable in a high state of purity, and can be used with a "dry-ice"-alcohol bath. Sing and Maddeley (1943) found it to be satisfactory for measuring the surface of silica gels. *n*-Butane was

* Defined as the ratio of equilibrium gas pressure (p) to saturation vapour pressure of the gas (p_0) at bath temperature. Sometimes represented as "X."

found to be satisfactory for aluminas by Russell and Cochran (1950), and it has been used for other adsorbents. It is more readily purified than ethane, and will cover a wide range of partial pressures, using an ice-bath. It possesses the disadvantage, however, that there is less agreement about the value to be assigned to the molecular cross-section than is the case with the other gases mentioned (Russell and Cochran, 1950; Livingston, 1949). A few runs were also made with oxygen, using the liquefied gas as cooling bath, some with ethane at -78°C , and one isotherm was obtained for carbon dioxide at the same temperature.

EXPERIMENTAL

Apparatus

In principle, this follows the set-up outlined by Nelson and Hendricks (1943), and a general photograph is shown in Fig. 1. Special features which have been introduced are:

- (a) The sample container (see Figs 1 and 2) of volume about 4.5 ml has a flat base enabling the sample to be spread out. This minimizes the tendency for particles to be carried upwards and thus block the $\frac{1}{2}$ -mm-diameter capillary during the initial evacuation. As a further precaution against blockage by particles adhering to tap grease, the portion of the stem adjacent to the tap is 2 mm diameter. The spout for introduction of the sample was ground to a slight taper and closed with a removable cap, the joint being lubricated with silicone grease. For mercury-sealed taps, and for the tap on the sample container, Dow-Corning silicone lubricant was used, and "L" type Apiezon tap lubricant (Metropolitan-Vickers Co.) for the remainder, which were previously ground in with 500-mesh carborundum and glycerol paste.
- (b) The connecting tube is 1 mm capillary to about 1 cm above the constant mercury level on the short arm of the manometer, which is made from 1 cm inside diameter "true-bore" tubing. The volume of apparatus thus exposed to ambient temperature is about 4 ml.
- (c) The volumes of the bulbs are 4.12, 5.22, 7.52, 11.52, and 19.27 ml, in sequence from top to bottom. These volumes give conveniently spaced adsorption points for a 1 g sample having a surface of the order of 100 sq. metres per gram. For adsorbents of greater or less surface area, the size of sample was selected accordingly.
- (d) Mercury reservoirs for the manometer and gas burette are readily removable for cleaning out these parts as required.



FIG. 1.—Gas adsorption apparatus, general view.

Materials.

GASES

Nitrogen was taken from cylinders supplied by New Zealand Industrial Gases Ltd. It was purified from oxygen by heated copper turnings and alkaline pyrogallol, and dried by sulphuric acid and phosphorus pentoxide. Analysis of the purified gas by the Mass Spectrometer Section, Dominion Physical Laboratory, D.S.I.R., gave an oxygen content of 0.11%.

Argon was taken directly from cylinders, as supplied for "Argon-Arc" welding. A sample of this gas analysed by the mass spectrometer showed 98.3% purity, the remainder being nitrogen. "Spec-pure" grade argon, supplied in sealed flasks by the British Oxygen Co., Wembley, England, was also used.

Nitrous oxide, B.P. grade, was taken from cylinders and dried by phosphorus pentoxide. Check runs, using a sample of the gas solidified by liquid oxygen, showed that there was insufficient non-condensable impurity to affect the results.

n-Butane from "lecture" bottles, supplied by the Fisher Scientific Co., Pittsburgh, U.S.A., was dried over phosphorous pentoxide, liquefied at -5° to -10° C, and vaporized into evacuated glass bulbs.

Ethane from the same source as the butane was taken directly from the "lecture" bottle.

Helium, supplied by the Air Reduction Co., U.S.A., was passed over lithium metal at about 400° C, to remove impurities other than the inert gases. Unpurified helium gave "dead-space" values that were too high.

Oxygen, B.P. grade, was taken directly from cylinders.

Carbon dioxide was taken directly from cylinders of liquefied gas, supplied by New Zealand Carbonic Ice Ltd. Where gases were collected in evacuated glass bulbs without previous condensation, a pressure of a few centimetres of water was maintained in the connecting tubing by means of a bubbler in order to prevent air from being drawn in through the cylinder reduction valve.

ADSORBENTS

Soil samples S479 and S715: These are subsoils derived from the Tirau Ash Shower, near Whakamaru Hydroelectric Station, New Zealand. Both samples contain large amounts of allophane (Birrell and Fieldes, 1952).

Soil 6168: Soil from Aitutaki Island, Cook Islands. This soil was reported (Dr P. G. Harris, pers. comm.) to contain the amorphous hydration product of basaltic glass, commonly known as palagonite, and consisting chiefly of the hydrous oxides of silicon, aluminium, and iron.

Soil S280: Hydrothermally altered heavy clay from Rotorua, New Zealand. Contains kaolin and montmorillonite (Gradwell and Birrell, 1954).

Olinda soils: Subsoils of a soil from the "Latosolic Brown Forest Group" from Maui Island, Hawaii, supplied by Dr G. D. Sherman, of the University of Hawaii. These soils contain much amorphous material (M. Fieldes, pers. comm.).

Ignited gibbsite: Prepared by heating to 750°C a mineralogical specimen supplied by Dr P. G. Harris, Department of Geology, University of Leeds, England. The alumina prepared in this way was found to have a fairly reproducible surface area.

Procedure

EXPERIMENTAL DETAILS

Samples were degassed at room temperature except where otherwise stated. For the samples of highest surface area, this required a period of up to 7 days under a vacuum of 10^{-5} mm mercury. The process was regarded as complete when, on isolating the sample from the pumps, the pressure in the apparatus did not rise beyond 10^{-3} mm mercury in one half-hour. With some soils, accelerated degassing by heating the sample to temperatures around 100°C was found to decrease the surface by as much as 25%; with others, there was no appreciable change. When more than one gas was used in successive runs on the same sample, degassing between runs was carried out overnight at room temperature.

It was generally found convenient to add successive increments of gas from the storage bulb until an equilibrium pressure of about 30 cm mercury had been reached with all calibrated bulbs empty, and then to



FIG. 2.—Sample container.

increase pressures by filling these bulbs with mercury in succession. Liquid oxygen was used as a cooling bath in experiments with nitrogen and argon, powdered "dry-ice" and alcohol with nitrous oxide, ethane, and carbon dioxide, and melting ice with *n*-butane. "Dead space" volumes were obtained with the purified helium gas at 0° C. Some "dead space" volumes were also calculated from specific gravity values of the oven-dried adsorbent as given by the water-displacement method. The maximum difference was found to 0.03 ml, which does not introduce a significant error in the surface area values. Owing to the difficulty of keeping purified helium ready for use over long periods of time, this latter method may be preferable. Results published by Gradwell (1955) indicate that the maximum error introduced by using the water-displacement specific gravity for computing "dead space" would occur with soils consisting almost exclusively of allophane and would amount to about 0.02 ml for a 0.5 g sample in the gas adsorption apparatus.

Practical limits of partial pressures obtainable with the apparatus and the vapour pressures of the gases at cooling bath temperature are given in Table 1.

TABLE 1.—Maximum Partial Pressures and Saturation Vapour Pressures of Gases Used.

Gas	Max. p/p_0	Vap. press. (cm of Hg)
Nitrogen	0.25	268.9
Argon	0.60	101.6
Nitrous oxide	0.45	142.5
Ethane	0.50	129.1
<i>n</i> -Butane	0.75	77.5
Carbon dioxide	0.85	76.0

It was assumed that the liquid oxygen was at -183°C , and the "dry-ice" alcohol paste at -78.1°C . The vapour pressure values in the above table were obtained from the International Critical Tables, with the exception of the value for *n*-butane at 0° C, which is the value given by Dana *et al.* (1926).

About one hour usually elapsed between the time that the liquid oxygen was drawn off from the tank at the factory and the beginning of a test run. Its temperature therefore would be very close to the normal boiling-point.

Results were corrected for gas-law deviation. In the case of butane, the volume of gas in the bulbs and connecting tubing was corrected as well as the "dead-space" volume. The correction values used were those given by Emmett and Brunauer (1937a). For ethane, where no correction figure was available, the value was assumed to be the same as for nitrous oxide, on account of the closeness of the boiling-points of the two gases.

Satisfactory equilibrium was obtained with nitrogen, argon, and oxygen within one half-hour after adding gas, or compressing the gas already in the system. For butane and ethane, one hour was found to be sufficient, but nitrous oxide required up to two hours with some soils, and even longer with the Rukuhia peat. Carbon dioxide behaved similarly to nitrous oxide. However, readings were taken after two hours when using these gases with the Rukuhia peat, in order to avoid prolonging the experiment unduly.

CURVE-FITTING PROCEDURE AND CALCULATIONS

The procedure for calculating surface areas from the experimental data follows the well-known multimolecular adsorption theory of Brunauer (1945a), who proposed the general equation:

$$V = \frac{V_m CX}{1 - X} \cdot \frac{1 - (n + 1)X^n + nX^{n+1}}{1 + (C - 1)X - CX^{n+1}},$$

connecting V the volume of gas adsorbed, X the partial pressure, and V_m the volume sufficient to form a monolayer on the adsorbent, n and C being constants. The method of Joyner, Weinberger, and Montgomery (1945) was used to obtain the value of n that best fitted the experimental results. For values of n greater than 3.0, it was found sufficiently accurate to select the most suitable value of n from the range 4.0, 5.0, or infinity. For n infinite, the general equation becomes

$$\frac{X}{V(1 - X)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} X,$$

which previous workers have regarded as accurate enough for measuring surface areas of soils and soil colloids by gas adsorption. The justification for making use of the method of Joyner *et al.* in the present investigation was that, for the lower values of n at least, the change in surface area values was greater than the experimental error.

From the V_m value obtained, the surface area (S) in square metres per g was calculated as follows:

$$S = \frac{6.02 \times 10^{23} \times V_m \times a \times 10^{-20}}{22,400W'} = \frac{0.269V_m a}{W'}$$

where a = cross-section of the gas molecule in square Angstrom units, and W = weight of sample after drying at 105°C . The cross-section areas used were those considered by Livingston as the "best" values.

Isotherms for argon, butane, and oxygen given by the soils usually conformed to the sigmoid shape characteristic of Brunauer's (1945a) type II isotherm. Those for carbon dioxide and ethane did not conform so well. Nitrogen and nitrous oxide isotherms could not be carried far enough to establish their true shape.

With butane, the plot of

$$\frac{X}{V(1-X)}$$

against X remained fairly straight up to X values of 0.3 or 0.4, whereas, with the other gases, a curvature convex to the X axis usually started below an X value of 0.3. In the light of results obtained by Russell and Cochran (1950) for butane adsorption by aluminas, this is consistent with the low " C " values obtained for soils with this gas.

DISCUSSION OF RESULTS

From Table 2, the following observations regarding surface areas can be made:

- (1) Argon gives satisfactory agreement with nitrogen, and the gas from commercial cylinders is pure enough for the purpose.
- (2) Nitrous oxide, and carbon dioxide also, give much higher values than argon for the soils. The ratio between nitrous oxide and argon surfaces is, however, not constant. On the other hand, good agreement is obtained between nitrous oxide and argon for ignited gibbsite.
- (3) For the soils, butane (if assumed to have a cross-section of $44.6\text{\AA}^2$) gives higher values than argon, but lower values than nitrous oxide. An exception is the Olinda soil (28 in. to 40 in. horizon) which had been heated to 100°C , where there is apparent agreement between the two values. The butane value for ignited gibbsite is higher than the argon value. How-

TABLE 2.—Surface Areas by Gas Adsorption (runs made in the order given).

Adsorbent	Gas	Surface m ² g	Max. p/p_0	n value for best fit	C	p/p_0 at V_m
Soil S479, fraction less than 2μ , first sample. Organic carbon content of whole soil, 1.36%	Nitrogen	356	0.21	∞	60	0.11
	Argon	358	0.55	3.5	36	0.15
	Argon	345	0.61	4.0	41	0.13
	Nitrogen	335	0.23	∞	78	0.10
Soil S479, fraction less than 2μ , second sample	<i>n</i> -Butane	393	0.72	3.0	7.6	0.26
	Argon	314	0.56	3.0	35	0.14
Soil S715, fraction less than 2μ	Nitrous oxide	364	0.35	4.0	28.6	0.16
	Argon	263	0.53	3.0	22	0.17
Soil S715, fraction less than 20μ	<i>n</i> -Butane	175	0.70	4.0	9.8	0.25
	Argon	161	0.50	3.0	21	0.19
	Oxygen	147	0.58	3.0	16.2	0.22
	Nitrous oxide	245	0.39	3.0	21	0.18
	Nitrous oxide	245	0.37	2.0	21	0.21
Soil 6168. Organic carbon 1.35%	Nitrogen	96	0.13	∞	102	0.09
	Nitrous oxide	144	0.34	3.0	34	0.155
Soil S280. Organic carbon 0.2%	<i>n</i> -Butane	76	0.38	∞	9.1	0.25
	Argon	57	0.30	∞	31.	0.15
	Nitrous oxide	70	0.40	∞	23	0.175
Olinda soil 16 in. to 28 in. pretreated with H ₂ O ₂ . Organic carbon 6.9%	<i>n</i> -Butane	66	0.73	5.0	6.8	0.27
	Argon	46	0.55	∞	29	0.16
Olinda soil, 28 in. to 40 in. Organic carbon 8.6%	<i>n</i> -Butane	46	0.76	5.0	11.3	0.21
	Argon	36	0.63	2.8	34	0.15
	Ethane	57	0.50	2.5	16	0.22
Olinda soil, 28 in. to 40 in. pretreated with H ₂ O ₂ . Organic carbon 3.5%	Argon	194	0.43	3.0	32	0.15
	Nitrous oxide	272	0.36	3.0	31	0.16

As above, but surface measured two months later	Ethane	163	0.44	2.5	13	0.24
	Nitrous oxide	234	0.33	4.0	27	0.16
	Argon	148	0.52	4.0	29	0.16
	Argon (specpure)	143	0.30	3.0	38	0.15
Olinda soil, 28 in. to 40 in., after shaking with 1.5N neutral lithium acetate solution. First preparation. Surface measured immediately. Organic carbon 10.8%	<i>n</i> -Butane	183	0.80	4.0	15	0.19
	<i>n</i> -Butane	99	0.64	4.0	25	0.17
	Nitrous oxide	169	0.29	4.0	61	0.13
	Oxygen	83	0.60	3.0	21	0.16
As above, but surface measured two months later	Argon	64	0.44	5.0	64	0.12
	Argon (specpure)	65	0.31	∞	63	0.12
	Argon	35	0.60	4.0	19	0.18
	Oxygen	35.5	0.45	4.0	24	0.16
Second preparation, as above—Surface measured one month later	<i>n</i> -Butane	67	0.53	4.0	9.8	0.24
	Nitrous oxide	72	0.75	5.0	12.5	0.22
	Argon	122	0.35	∞	52	0.12
		46.5	0.57	5.0	71	0.18
Second preparation, as above. Degassed at 100° C. Surface measured one month later	Nitrous oxide	110	0.40	4.0	66	0.12
	Argon	49	0.53	3.0	33	0.15
	<i>n</i> -Butane	48	0.76	5.0	13.5	0.20
Gibbsite, ignited at 750° C, first preparation	Nitrous oxide	126	0.37	∞	30	0.15
	Argon	119	0.43	4.0	22	0.17
Gibbsite, ignited at 750° C, second preparation	<i>n</i> -Butane	134	0.45	∞	7.4	0.27
	Argon	114	0.34	∞	27	0.16
	Nitrous oxide	113	0.33	∞	19.8	0.18
Olinda soil, 28 in. to 40 in., after shaking with 1.5N neutral lithium acetate solution (composite sample). Degassed at 100° C	Carbon dioxide	92.5	0.68	3.0	24	0.17
	Nitrous oxide	120	0.41	3.0	38.4	0.13
	Argon	41	0.46	4.0	35.6	0.14
	Ethane	105	0.42	3.0	7.6	0.30
Rukuhia peat	Argon	0.8	0.53	∞	18	0.12
	Ethane	4.4	0.24	∞	4.3	0.35
	<i>n</i> -Butane	10.5	0.55	∞	4.2	0.25
	Nitrous oxide	42+	0.16	∞	34	0.15
	Carbon dioxide	29+	0.31	∞	15	0.20

ever, Russell and Cochran (1950) found that for aluminas good agreement between butane and nitrogen surface areas was obtained if the cross-sectional area of the butane molecule was taken as $39\text{\AA}^2$ relative to nitrogen as $16\cdot2\text{\AA}^2$. This is equivalent to $37\text{\AA}^2$ for butane relative to nitrogen as $15\cdot4\text{\AA}^2$, the latter being the figure selected by Livingston (1949) for nitrogen. With this change, butane and argon values for ignited gibbsite would agree well, but there would still be large and varying differences for the soils. It would also be necessary to postulate some decrease in pore size as a result of heating the Olinda soil mentioned above, but this is not improbable (Brunauer, 1945b).

- (4) Ethane does not appear to be as satisfactory as argon, although it is better than nitrous oxide. The sample used does not show any marked advantage over butane.
- (5) Oxygen gives better estimates of the surface areas of soils than butane, even when the organic matter content is quite appreciable.
- (6) The results in Table 2 would suggest that the unsatisfactory results with nitrous oxide and carbon dioxide are due to the presence of organic matter in the soils, and there appears to be a general relationship between the ratio of nitrous oxide surface to argon surface and organic carbon content. Further, it was noted that organic matter slowed up the rate of adsorption of nitrous oxide and carbon dioxide. Although the evidence is less definite, it is possible that soil organic matter may have some effect on the surface area values obtained with butane and ethane.

Experimental results not included in Table 2 showed that successive adsorption runs with nitrous oxide were generally reproducible within a few per cent. if the gas was pumped off at room temperature overnight. With the Rukuhia peat, the change in adsorptive capacity was rather more marked. On the third run for nitrous oxide with this adsorbent, the volume of gas adsorbed at a given partial pressure had dropped by about 15%. However, even this decrease is of a small order compared with the changes in adsorptive capacity observed by Emmett and Brunauer (1937b) when studying cases in which chemisorption effects occurred. The adsorptions of nitrous oxide at 20°C and 67°C by the Olinda soil sample of 10.8% organic carbon content could be fitted to the isotherm for this gas at -78°C , if the appropriate p_0 values for the gas at these temperatures were used, so that there is no apparent reaction at these higher temperatures.

The deduction can reasonably be made from these results, therefore, that chemisorption does not play an important part in causing the abnormally high adsorption of nitrous oxide by soils containing organic matter.

Some observations were made on hysteresis effects as indicated by comparisons between the volumes of gas adsorbed in adsorption and

desorption runs. For nitrogen and argon, the difference was between 1% and 2%; for butane 5% to 8%; and for nitrous oxide about 6%. There was also some retention of nitrous oxide observed when the gas was pumped off the adsorbent at -78°C overnight, under high vacuum. This was of about the same order as the hysteresis effect.

HEATS OF ADSORPTION

These are shown in Table 3 for the gases used, excluding the results obtained with Rukuhia peat which were rather less accurate than those for the other adsorbents. The heat values were obtained according to Brunauer's (1945a) procedure using the maximum value of "*C*" for the particular gas, as given by the general equation quoted earlier. The heats of adsorption are all of the correct order for physical adsorption, and those shown for nitrogen agree with values found by Makower, Shaw, and Alexander (1937), using this gas with soil adsorbents.

TABLE 3.—Heats of Adsorption Data for Soils.

Gas	Maximum C value	Average C value	$E_i - E_L$ cal./mole	E_i cal./mole
Nitrogen	102	80	825	2155
Argon	71	33	760	2265
Nitrous oxide	66	37.5	1425	4375
Oxygen	24	20.4	566	2420
<i>n</i> -Butane	25	11.7	1720	7040
Ethane	13	—	990	5060

CONCLUSIONS

- (1) Argon, as supplied for commercial welding, is equally as suitable as nitrogen for determining the surface areas of soils and soil colloids.
- (2) Butane is suited for obtaining approximate estimates of surface only.
- (3) Both nitrous oxide and carbon dioxide are unsuitable for measuring soil surface areas.
- (4) If no swelling clay minerals are present, specific gravity values obtained by the water displacement method may be used for calculating dead space volumes in lieu of direct determinations with helium at 0°C .
- (5) Commercial ethane does not appear to be a satisfactory substitute for argon.

ACKNOWLEDGEMENTS

Thanks are due to Mr C. C. Hensen, Dominion Laboratory, for making the glass parts of the apparatus; to Mr L. C. Blakemore, Soil Bureau, for organic carbon determinations; and to Miss J. B. Ross, Dominion Laboratory, for samples of hydrocarbon gases.

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NUTRITIONAL STUDIES OF *PHYTOPHTHORA* *CACTORUM* (LEB. AND COHN) SCHROET

PART I: UTILISATION OF NITROGEN AND CARBON COMPOUNDS

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(Received for publication, 17 July 1957)

Summary

A number of substances containing nitrogen were tested as sole sources of nitrogen, for growth by *P. cactorum* with dextrose as a carbon source. Where no adjustment was made in the initial pH of the media the amino acids, arginine, histidine, and threonine were the best sources of organic nitrogen and $\text{Ca}(\text{NO}_3)_2$ the best source of inorganic nitrogen.

With the initial pH of the media adjusted to 6.5 the best sources of organic nitrogen were histidine, pepsin, and arginine and $\text{Ca}(\text{NO}_3)_2$ was again the best source of inorganic nitrogen.

Nine carbon compounds were tested as sole sources of carbon with NaNO_3 as the nitrogen basis. With no adjustment of the initial pH and with the initial pH of the solutions adjusted to 6.5 sucrose and maltose were the best sources of carbon.

Four calcium compounds added singly to the basal medium gave no increase in the growth of the fungus.

Iron added to the basal medium in the form of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ at a concentration of 4 p.p.m. depressed the growth of the fungus.

INTRODUCTION

In recent years some attention has been paid to the nutrition of species of *Phytophthora*. Wills (1954), studying the utilisation of carbon and nitrogen compounds by an isolate of *P. parasitica* var. *nicotianae*, found that the amino acids, histidine, threonine, and ornithine, were the best source of nitrogen, and that dextrin and starch were the best utilised of the carbon compounds tested. Lopatecki and Newton (1956) examining the nutrition of several species of *Phytophthora*, including an isolate of *P. cactorum*, obtained evidence suggesting that all *Phytophthora* species made better growth in nutrient solutions containing an organic sources of nitrogen than in those with an inorganic source of nitrogen. Roborgh (1956) has suggested that the heavy incidence of the black root-rot disease of the hop, caused by *P. cactorum*, in commercial hop gardens is linked with the organic ingredients, dried blood and meat and bone, contained in the fertiliser mixture generally used.

An examination of some of the nutrient needs of a strain of *P. cactorum*, isolated from a dead hop plant, is described hereunder.

The same strain of the fungus was used as has been described previously (Christie 1956).

MATERIALS AND METHODS

Stock cultures of the fungus were maintained on potato-dextrose agar at room temperature.

A basal culture medium of the following composition was used: NaNO_3 , 2g; KH_2PO_4 , 2g; KCl , 0.5g; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5g; dextrose, 30g; distilled water, 1000ml; and thiamine hydrochloride, 25p.p.m. All chemicals used were of standard analytical reagent grade. Preliminary trials showed that in the above medium with thiamine omitted no growth was made by the fungus.

The nitrogen and the carbon compounds tested were substituted singly for NaNO_3 and for dextrose in the above medium in quantities sufficient to maintain the nitrogen and the carbon at the same level as in the basal medium. Exceptions to the above substitution of carbon were, soluble starch which was tested at two concentrations, 30g and 8g per 1000ml of solution, and inulin at 8g per 1000ml.

In the studies of the effect of calcium compounds upon the growth of the fungus the compounds tested were added singly to the basal medium in amounts necessary to maintain the calcium at the same level as provided by the substitution of $\text{Ca}(\text{NO}_3)_2$ for NaNO_3 in the basal medium.

The cultures of the fungus were grown in 50ml of the solution in 250ml Erlenmeyer flasks. For each substance tested there were five replicates. All flasks used were cleaned in a sulphuric acid-potassium dichromate solution and well washed in distilled water. All solutions were autoclaved at 15 lb. pressure for 15 min.

For each source of nitrogen, carbon, and calcium, pH determinations of the solutions were made before inoculation of the flasks and at the end of the growth period. Since preliminary experiments showed that the optimum pH for growth in the basal medium lay between 6.0 and 7.0 a second series of tests involving the same sources of nitrogen and of carbon, but with the pH of the solutions adjusted to 6.5 before the inoculation of the flasks, was instituted, and pH determinations made again at the end of the growth period.

A standard inoculum measuring 3mm square of the fungus growing on potato-dextrose agar, the smallest amount of inoculum that could conveniently be handled and which by tests gave consistent growth of the fungus, was introduced into each flask.

After inoculation the flasks were placed in an incubator and maintained for 17 days at 23°C . In the series comparing three inorganic nitrogen compounds as sources of nitrogen with and without the addition of iron to the media, growth was maintained for 38 days at room temperature.

The amount of growth was determined by weighing the dried mycelium from each flask. At the end of the growth period the mycelium from each flask was filtered on tared filter paper, thoroughly washed with distilled water and dried in an oven at 60°C for 24 hr. The weights recorded represent the mean weight of the five replicates of each substance tested.

GROWTH OF *P. CACTORUM* IN THREE INORGANIC SOLUTIONS WITH AND WITHOUT THE ADDITION OF IRON TO THE MEDIA

Iron was omitted from the basal medium because it was considered that this element was present as an impurity in sufficient amounts to meet the needs of the fungus. To determine whether this was the case or not three inorganic sources of nitrogen, NaNO_3 , $\text{Ca}(\text{NO}_3)_2$, and KNO_3 , at the same level as in the basal medium, were tested at room temperature as sources of nitrogen with and without the addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to the media at a concentration of 0.004g per 1000ml. Growth was maintained for 38 days. Determinations of the pH of the solutions were made at the end of the growth period. The results of this test are shown in Table I.

TABLE 1.—Growth of *P. cactorum* in a Basal Medium With Three Differing Inorganic Sources of Nitrogen, With and Without the Addition of Iron to the Media.

Source of nitrogen	pH of solution at beginning of growth period	pH of solution at end of growth period	Weight of mycelium (mg)
$\text{Ca}(\text{NO}_3)_2$	4.3	5.5	310
$\text{Ca}(\text{NO}_3)_2 + \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	4.0	5.3	237
NaNO_3	4.7	5.9	197
$\text{NaNO}_3 + \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	4.5	5.7	143
KNO_3	4.7	5.9	178
$\text{KNO}_3 + \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	4.6	5.8	130

The addition of iron to each of the above media had the effect of depressing the growth of the fungus and bringing about an increase in the acidity of the media at the beginning and at the end of the growth period. Lopatecki and Newton (*loc. cit.*) found that with *P. parasitica* iron at a concentration of 2p.p.m. or higher depressed the growth of the fungus.

UTILISATION BY *P. CACTORUM* OF NITROGEN FROM VARIOUS INORGANIC AND ORGANIC SOURCES

Twenty-two substances containing nitrogen were tested as sole sources of nitrogen for growth by the fungus. Each compound was

added singly to the basal medium and NaNO_3 omitted. The results of these tests with no adjustment of the initial pH of the solutions and with the initial pH adjusted to 6.5 are presented in Table 2.

The amino acids, arginine, histidine, and threonine, were the best sources of organic nitrogen in the unadjusted media. Asparagine, peptone, ornithine, pepsin, and urea were well utilised. The remaining organic compounds were poorly utilised. The only inorganic compound that was well utilised was $\text{Ca}(\text{NO}_3)_2$.

With the media standardised at pH 6.5 the best growth was obtained with histidine as a source of nitrogen. Arginine, pepsin, peptone, asparagine, urea, threonine, and ornithine were well utilised. As with the unadjusted media the remaining organic compounds were not good sources of nitrogen. At this pH level $\text{Ca}(\text{NO}_3)_2$ was again well utilised.

UTILISATION BY *P. CACTORUM* OF CARBON FROM VARIOUS SOURCES

Nine carbon compounds were tested as sole sources of carbon. Eight compounds were added singly to the basal solution and dextrose omitted. The results of these tests with no adjustment of the initial pH of the solutions and with the initial pH adjusted to 6.5 are presented in Table 3.

In both media the disaccharide sugars, sucrose and maltose, were the best sources of carbon. The remaining carbon compounds were poorly utilised or not utilised.

EFFECT ON GROWTH OF *P. CACTORUM* OF THE ADDITION OF CALCIUM COMPOUNDS TO THE BASAL MEDIUM

The good growth of the fungus in the basal medium with $\text{Ca}(\text{NO}_3)_2$ as the substrate for nitrogen prompted an enquiry as to whether the presence of calcium in the solution might be responsible for this growth. Four calcium compounds, calcium sulphate, calcium oxide, calcium carbonate, and calcium acetate, were added singly to the basal medium in amounts sufficient to maintain the calcium level at the same figure as in the medium containing $\text{Ca}(\text{NO}_3)_2$.

With each of these sources of calcium added to the medium the growth of the fungus was poor. Some growth was made in the presence of calcium sulphate and slight growth took place with calcium oxide. Only a trace of growth was made with calcium carbonate and calcium acetate failed to give any growth of the fungus.

CONCLUSIONS

The increases in the weights of mycelium yielded by $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 as nitrogen substrates over a 38-day period of growth as

TABLE 2.—Growth of *P. cactorum* in a Basal Medium With Differing Sources of Nitrogen.

Source of nitrogen	Initial pH of solution	pH of solution at end of growth period	Weight of mycelium (mg)	Initial pH of solution	pH of solution at end of growth period	Weight of mycelium (mg)
L-arginine·HCl	4.9	3.8	291	6.5	4.3	154
L-histidine·HCl	4.5	4.3	257	6.5	4.7	220
dl-threonine	4.9	3.8	159	6.5	5.5	86
Ca(NO ₃) ₂	4.3	4.9	159	6.5	5.5	157
asparagine	4.5	4.6	150	6.5	5.1	127
peptone	5.2	4.3	112	6.5	4.8	141
dl-ornithine·HCl	4.8	3.3	111	6.5	4.6	70
pepsin	3.8	3.5	97	6.5	4.3	163
urea	6.3	5.2	79	6.5	5.4	89
NH ₄ NO ₃	4.5	3.4	45	6.5	5.5	89
haemoglobin	5.4	4.8	37	6.5	5.9	63
(NH ₄) ₂ HPO ₄	6.9	5.9	33	6.5	5.6	27
edestin	5.0	4.7	33	6.5	6.2	11
casein	4.9	4.4	27	6.5	5.8	29
egg albumen	5.2	5.4	26	6.5	6.0	12
blood albumen	5.2	4.7	20	6.5	6.2	5
(NH ₄) ₂ SO ₄	4.6	3.4	19	6.5	4.6	47
NaNO ₃	4.7	4.7	16	6.5	5.7	67
gelatine	4.7	4.5	10	6.5	5.7	31
zein	4.6	no determination	no growth	6.5	5.8	16
KNO ₃	5.9	no determination	no growth	—	—	—
NaNO ₂	6.1	no determination	no growth	—	—	—

TABLE 3.—Growth of *P. cactorum* in a Basal Medium With Differing Sources of Carbon.

Source of carbon	Initial pH of solution	pH of solution at end of growth period	Weight of mycelium (mg)	Initial pH of solution	pH of solution at end of growth period	Weight of mycelium (mg)
sucrose	4.5	4.9	159	6.5	6.2	118
maltose	5.2	4.4	60	6.5	6.3	160
d-galactose	4.9	5.3	53	6.5	6.2	27
l-arabinose	4.5	4.6	33	6.5	no determination	no growth
soluble starch (30g/1000ml)	4.7	4.0	24	—	—	—
fructose	4.7	4.1	23	6.5	no determination	no growth
d-xylose	4.5	4.6	18	6.5	no determination	no growth
dextrose	4.7	4.7	16	6.5	5.7	67
soluble starch (8g/1000ml)	4.7	4.1	10	6.5	6.5	2
inulin	4.8	4.2	7	6.5	6.2	18

compared with a 17-day period, suggest that with the longer period more complete utilisation of the substrates has taken place. The shorter growth period was arbitrarily determined since no information is available of the optimum period for growth by this fungus under conditions of artificial culture.

The evidence from the tests over the 17-day period at a constant temperature suggests that this species of *Phytophthora* is better able to utilise organic sources of nitrogen than inorganic sources. At both pH levels the amino acids were good sources of nitrogen. The degree of utilisation of other organic nitrogen compounds varied, some being well utilised at both levels and others less well utilised or only poorly so. Of the inorganic nitrogen compounds examined only $\text{Ca}(\text{NO}_3)_2$ gave growth comparable with that given by the amino acids. No evidence was obtained to suggest that the presence of calcium in the medium was responsible for this good growth. Neither NaNO_2 nor KNO_3 were available to the fungus in the unadjusted media. No tests were made with these compounds at the higher pH level.

The differences in the utilisation of the nitrogen compounds according to the pH of the solutions suggest that growth of the fungus in solutions of this nature is influenced by the hydrogen-ion concentrations of the media. The degree of acidity of the solutions appears to be a factor in determining how well the amino acids are utilised. In the less acid solutions these were less well utilised.

Other organic compounds, pepsin, peptone, and urea, showed the opposite tendency: utilisation of these compounds was better in the less acid media. Zein was not utilised in the more acid solution: in the less acid solution some growth of the fungus was made.

Although maltose and sucrose proved to be the best sources of carbon of the compounds tested the availability of these compounds to the fungus was influenced also by the hydrogen-ion concentrations of the media. The same influence of pH was evident in the solutions containing l-arabinose, d-xylose, and fructose which were not available to the fungus in the less acid solutions.

The varying growths made by the fungus in solutions with different sources of nitrogen and carbon suggest that availability to the fungus of both nitrogen and carbon may be influenced by the types of nitrogen and carbon compounds present in the media.

As a result of these studies a synthetic medium for further investigations of the nutritional requirements of this species of *Phytophthora* has been prepared containing $\text{Ca}(\text{NO}_3)_2$ as a nitrogen source and sucrose as a carbon source.

ACKNOWLEDGEMENTS

The author is indebted to Mr R. J. Monk for the pH determinations and the adjustment of the pH of the solutions. Thanks are due to the Biochemical Department, Otago Medical School, for kindly supplying zein for use in these studies.

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SULPHUR ISOTOPIC VARIATIONS IN NATURE

PART 4—MEASUREMENT OF SULPHUR ISOTOPIC RATIO BY MASS SPECTROMETRY

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(Received for publication, 23 December 1957)

Summary

A mass spectrometer using double collection and rapid sample switching is described. Details of its use for sulphur isotopic measurements are given. This instrument can measure isotopic ratios of gas samples with an accuracy of 0.1 to 0.2‰ while the standard deviation of comparison measurements is 0.2‰.

A comparison of the New Zealand sulphur standard with standards used by other workers has been made.

INTRODUCTION

The sulphur isotope ratios of a number of sulphur samples of different origins have recently been determined at this laboratory (Rafter, 1958). These measurements were made on a Nier 60° sector-type mass spectrometer designed by Mr G. Page and constructed at Dominion Physical Laboratory. Originally the mass spectrometer was designed for single-collection methods, but to increase the accuracy of measurement it has since been modified by the authors for double collection and for rapid sample switching. This instrument does not measure absolute isotopic ratios but only differences in ratios.

THE SAMPLE SYSTEM

The sample system is based on that used by McKinney *et al.* (1950) and is shown schematically in Fig. 1. The sample to be analysed and the standard against which it is to be compared are attached to two separate manifolds. These manifolds are identical, except that attached to the standard manifold is a mercury column, by means of which the pressure of the standard behind the leak is adjusted to be the same as that of the sample. The leaks consist of 14 in. lengths of 0.006 in. inside diameter Nickel tubing, which ensures that conditions are sufficiently close to viscous flow for the isotopic composition of the standard sample to remain constant throughout one working day. By means of a solenoid operated valve (Wanless and Thode, 1953) it is possible to introduce the standard and the sample in rapid succession into the mass spectrometer ion source. This valve is so designed that while the gas from one inlet is flowing into the ion source the gas from

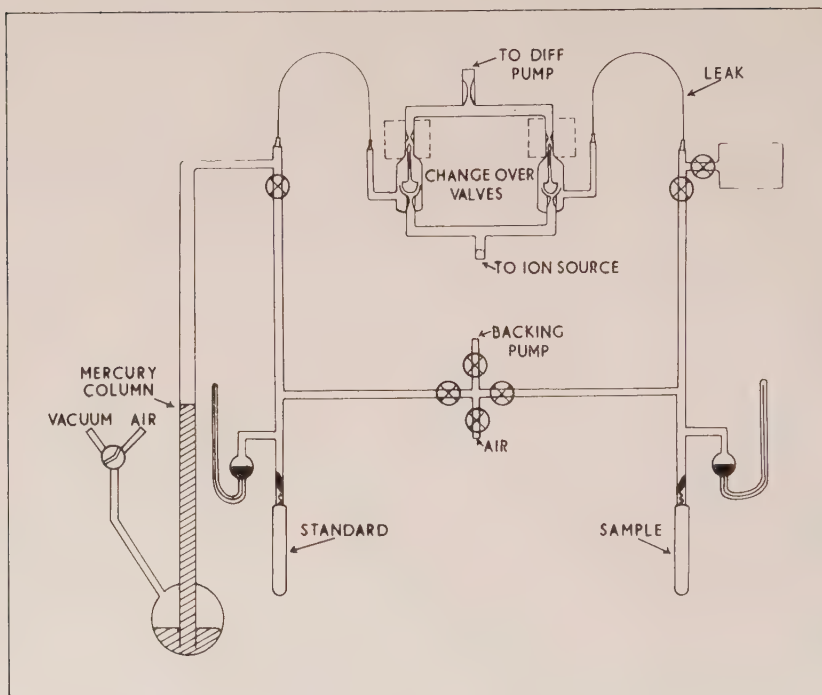


FIG. 1.—The Sample System.

the other inlet is flowing through a constriction to the waste line. For construction of the valve it was found most satisfactory to use as the main seal a commercial ball-and-socket joint. The slight leak-through of these valves when samples of natural abundance are being measured has no significant effect.

THE MASS SPECTROMETER TUBE

Glass envelope ends on the mass spectrometer tube are joined by Kovar seals to the copper centre tube which supports the ion source and ion collector. The ion source is constructed of Nichrome V with pyrex spacers and, except for the method of mounting, follows the design of Nier (1947).

The construction of the double collector (Fig. 2) is perhaps unique in that one of the collectors can be moved relative to the other so that the machine may be used for gases other than sulphur dioxide without the disadvantages of using a wide slit to collect the main beam.

The assembly consisting of the lower slit, secondary electron repeller, and collector can be moved from outside the tube by rotating mag-

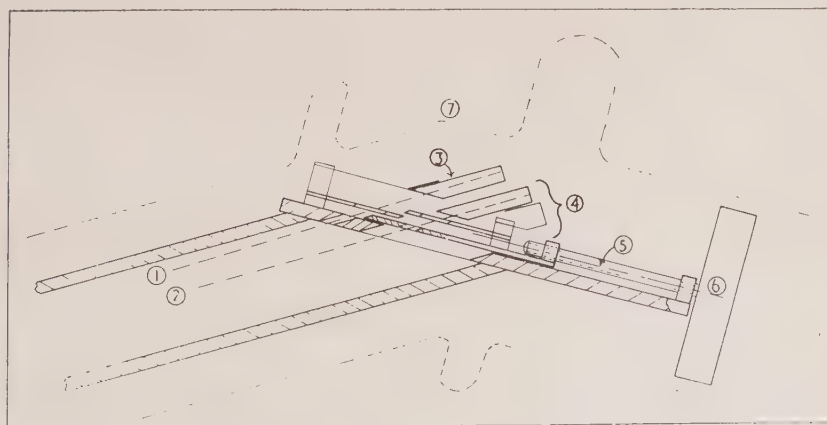
netically the bar of magnetic stainless steel which drives a lead screw connected to the assembly.

The only disadvantage of using this type of double collector is that it is not possible to change quickly from mass 45/mass 44 ratios to mass 46/mass 44 ratios when measuring carbon dioxide samples.

THE VACUUM SYSTEM

The high vacuum system is pumped by a fast single-stage mercury diffusion pump backed by a three-stage mercury diffusion pump which is in turn backed by a two-stage rotary pump. The glass cold trap between the mass spectrometer tube and the diffusion pumps is cooled by both liquid oxygen and dry ice. A dry ice and alcohol mixture is held in a large Dewar flask surrounding the trap and liquid oxygen in an inner tube built into the trap. A single filling of liquid oxygen lasts only about ten hours but a single filling of dry ice will last three days and thus does not require attention during a weekend.

An electromagnetic valve is connected between the diffusion pumps and the rotary backing pumps so that if the power fails the valve closes and air does not leak into the system through the backing pumps. At the same time a relay switches the diffusion pump heaters from the A.C. supply to a 36V bank of storage batteries. The diffusion pumps then pump into a backing reservoir. By this technique power cuts of up to four hours can be accommodated. When the power comes



1. Mass 64 beam
2. Mass 66 beam
3. Fixed collector

4. Movable Collector Assembly
5. Lead Screw
6. Magnetic Stainless Steel Bar

7. Glass Envelope

FIG. 2.—Construction of the Double Collector System.

on again the rotary pumps start and the diffusion pumps revert to the A.C. supply. Opening of the electromagnetic valve is, however, delayed for approximately a minute to allow the rotary pump pressure to come down to the operating point.

This automatic switching procedure prevents loss of operation time for, if air at atmospheric pressure remained in the main vacuum system for any length of time, several days' pumping would be necessary to attain the best vacuum.

If a leak sufficiently large to raise the backing pressure above 200μ develops in the vacuum system, a Pirani gauge control unit turns off the diffusion pump heaters.

If the cooling water supply to the diffusion pumps fails, a water switch disconnects the heater voltage so that mercury vapour does not distil throughout the vacuum system.

The control unit for the ionisation gauge includes a relay and interlock circuit so that, should the pressure rise above 10^{-5} mm of Hg, the source filament current and the ion accelerating voltage are cut off. This procedure prevents burn out of the source filament and electrical breakdown between the accelerating electrodes.

The electron emission from the source filament is controlled by means of a regulator similar to that described by Hutchison and Wolff (1954) which uses a 1400 c.p.s. square wave signal to heat the filament. The emission current controls the screen grids of the power amplifier tubes which are transformer coupled to the filament. The use of the 1400 c.p.s. voltage prevents the filament cooling between cycles, as occurs when 50 c.p.s. (mains frequency) heating voltage is used. This regulator keeps the emission constant to better than 0.1%. Pressure in the high vacuum system in the range of 10^{-5} to 10^{-8} mm of Hg is measured by the ionisation gauge control unit. This control unit is of standard design. The gauge emission is regulated by two power tubes which control the current to the filament transformer. The large changes in the filament emission caused by some of the gases (e.g. SO_2) run through the mass spectrometer make a good emission regulator for the gauge essential. The various voltages required for the ion accelerating system are derived by a resistance voltage divider connected across a 3 KV regulated power supply. The current for the electromagnet is supplied by a current regulated supply, the output of which may be varied between 0 and 300 mA so that the mass range 1 to 150 can be covered using a fixed ion accelerating voltage.

The output of each of these two supplies does not change by more than 1 part in 10,000 over a half-hour period, irrespective of normal mains voltage changes.

The ions falling on the first collector (mass 64) are measured by a FP54 electrometer and a D.C. amplifier, and ions falling on the second collector (mass 66) by a vibrating reed electrometer. Using the circuit shown in Fig. 3 the mass 66/mass 64 ratio may be measured using

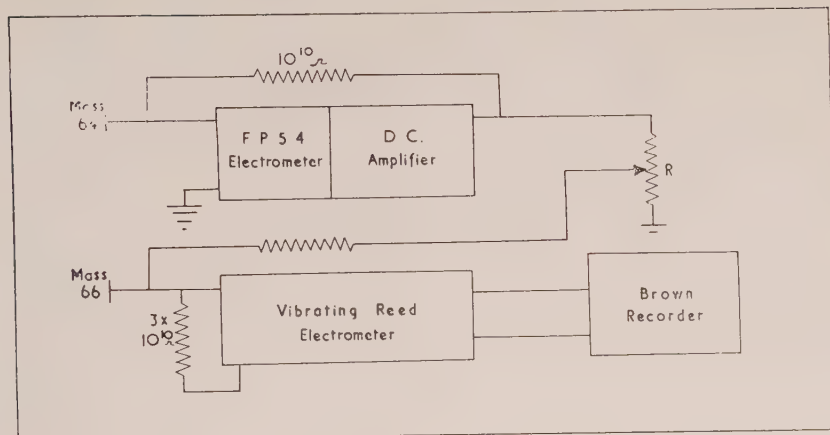


FIG. 3.—Ion Beam Ratio Measuring Circuit. For SO_2 samples, the second collector (mass 66) ion current input resistor has a value of 10^{11} ohms.

the decade resistance box R and a Brown Electronik recorder connected as the null indicator.

When the sample and the standard are admitted alternately into the ion chamber by means of the sample switching valves, the difference in their isotopic ratios appears directly on the recorder. In order to obtain good zero stability of the D.C. amplifier a 300-volt regulated power supply provides the high tension supply for the electrometer and amplifier tubes and runs the filament of the FP54 electrometer tube. This 300-volt source is also fed to the magnet regulator and the 3-KV supply to run the comparator tubes. A 250V regulated supply runs the 150 mA filaments of the first stages of the above units.

MEASUREMENT PROCEDURE

The method of measuring the isotope ratios is described below. With the sample flowing into the ion chamber, the decade resistance (R) (Fig. 3) is adjusted to bring the recorder trace as close as possible to the centre zero and is then left unaltered while a trace is drawn on the chart. The value of R used is noted beside the trace, together with the sample number, the output voltage (mass 64), and the mass spectrometer tube pressure. The sample valves are then changed over to allow the standard to flow into the ion chamber and the trace is recorded as before. The value of R is changed only if the difference between the sample and the standard is greater than 1 to 2%.

A sufficient number of traces, usually five or seven, are taken to ensure statistical accuracy of the results. A tracing of a typical chart is shown in Fig. 4. The sensitivity of the vibrating reed electrometer is such that the recorder reads approximately -10% to $+10\%$. A smoothed line is drawn through each trace and the difference from zero is used to correct the value of R. This corrected value is then a relative measure of the mass 66/mass 64 ratio.

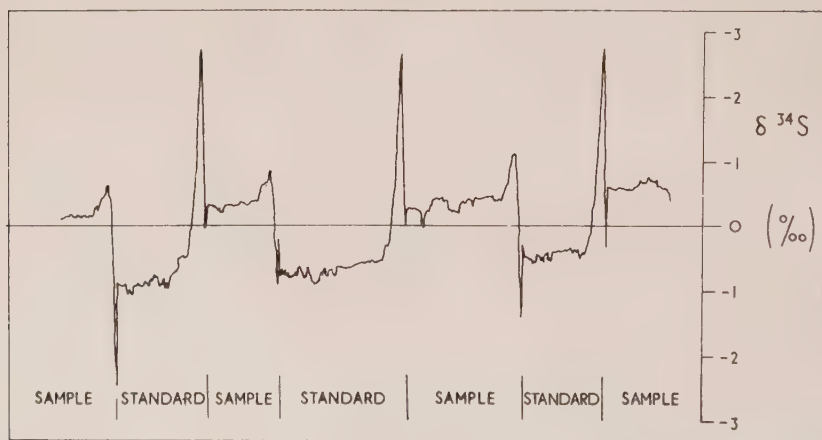


FIG. 4.—A copy of a Typical Recorder Trace.

CALCULATION OF δ VALUES

The results are usually expressed in terms of δ values, $\delta^{34}\text{S}$ being the difference between the $^{34}\text{S}/^{32}\text{S}$ ratio of the sample and of the standard, expressed in parts per thousand.

In the calculation of $\delta^{34}\text{S}$ values from the mass 66/mass 64 ratio, which follows, allowance is made for the presence of the oxygen isotopes in the sulphur dioxide molecule, as several combinations of oxygen and sulphur isotopes give mass 66 ions.

Thus

$$\begin{aligned} \frac{\text{Mass 66}}{\text{Mass 64}} &= \frac{{}^{34}\text{S}{}^{16}\text{O}{}^{16}\text{O} + 2 {}^{33}\text{S}{}^{17}\text{O}{}^{16}\text{O} + {}^{32}\text{S}{}^{17}\text{O}{}^{17}\text{O} + 2 {}^{32}\text{S}{}^{16}\text{O}{}^{18}\text{O}}{{}^{32}\text{S}{}^{16}\text{O}{}^{16}\text{O}} \\ &= \frac{{}^{34}\text{S}}{{}^{32}\text{S}} + 2 \frac{{}^{33}\text{S}{}^{17}\text{O}}{{}^{32}\text{S}{}^{16}\text{O}} + \frac{{}^{17}\text{O}{}^{17}\text{O}}{{}^{16}\text{O}{}^{16}\text{O}} + 2 \frac{{}^{18}\text{O}}{{}^{16}\text{O}} \end{aligned}$$

The actual values of the natural isotopic abundance of ^{33}S and of ^{17}O (0.74% and 0.04% respectively) are sufficiently small to be neglected in the calculation of the mass 66/mass 64 ratio.

Hence

$$\frac{\text{Mass 66}}{\text{Mass 64}} = \frac{{}^{34}\text{S}}{{}^{32}\text{S}} + 2 \frac{{}^{18}\text{O}}{{}^{16}\text{O}}$$

and thus

$$\frac{{}^{34}\text{S}}{{}^{32}\text{S}} = \frac{\text{Mass 66}}{\text{Mass 64}} - 2 \frac{{}^{18}\text{O}}{{}^{16}\text{O}} \quad \dots\dots\dots (1)$$

δ is defined by the relationship

$$\delta^{34}\text{S}\text{‰} = \frac{({}^{34}\text{S}/{}^{32}\text{S}) \text{ sample} - ({}^{34}\text{S}/{}^{32}\text{S}) \text{ standard}}{({}^{34}\text{S}/{}^{32}\text{S}) \text{ standard}} \times 1,000 \quad \dots\dots\dots (2)$$

$\delta^{34}\text{S}$ is thus the enrichment in ^{34}S of the sample with respect to the standard.

Let

$$\left(\frac{\text{Mass 66}}{\text{Mass 64}} \right) \text{ standard} = R \text{ std.} \quad ; \quad \left(\frac{\text{Mass 66}}{\text{Mass 64}} \right) \text{ sample} = R_x$$

$$\left(\frac{{}^{18}\text{O}}{{}^{16}\text{O}} \right) \text{ standard} = Q \text{ std.} \quad ; \quad \left(\frac{{}^{18}\text{O}}{{}^{16}\text{O}} \right) \text{ sample} = Q_x$$

Then from (1)

$$\left(\frac{{}^{34}\text{S}}{{}^{32}\text{S}} \right) = R \text{ std.} - 2 Q \text{ std.}$$

substituting in (2) we have

$$\delta^{34}\text{S} = \frac{R_x - 2 Q_x - (R \text{ std.} - 2 Q \text{ std.})}{R \text{ std.} - 2 Q \text{ std.}} \times 1,000$$

$$= \left[\frac{R_x - R_{\text{std}}}{R_{\text{std}} \left(1 - \frac{2 Q_{\text{std}}}{R_{\text{std}}} \right)} - \frac{2 (Q_x - Q_{\text{std}})}{2 Q_{\text{std}} \left(\frac{R_{\text{std}}}{2 Q_{\text{std}}} - 1 \right)} \right] \times 1,000 \quad \dots\dots\dots (3)$$

Substituting the values of

$$R_{\text{std}} = \frac{1}{22.1} \text{ and } Q_{\text{std}} = \frac{1}{490}$$

in the terms in parentheses in the bottom lines of eqn. (3) and defining δ (mass 66) and $\delta^{18}\text{O}$ in a similar way to $\delta^{34}\text{S}$ we obtain

$$\delta^{34}\text{S} = 1.09 \delta (\text{mass } 66) - 0.1 \delta^{18}\text{O}.$$

In order to make $\delta^{18}\text{O}$ negligible all samples and standards are burnt in oxygen from the same cylinder. It is considered that any fractionation of the oxygen isotopes in the burning process would be sufficiently constant between samples that the $\delta^{34}\text{S}$ value is not altered significantly.

SOURCES OF ERROR

Pressure Effects

With identical pressures behind the leaks the measured difference for the same sample in both manifolds is zero. When the pressure behind one leak was altered, the δ value changed by -4.5% , for a one-volt change in output of the D.C. amplifier. The source of this error was later determined as being due to incorrect positioning of the analysing tube in the magnetic field. In order, however, to obtain an accuracy of $\pm 0.5\%$ in the results; it was necessary to adjust the pressures behind the leaks so that the difference in peak voltage was less than 0.1 volt. In practice this was easily obtainable by adjustment of the mercury column on the standard manifold. Operation with equal mass 64 voltage also minimised the effect of zero shifts in the D.C. amplifier or in the vibrating reed. Later, after readjustment of the analysing tube in the magnetic field, the pressure effect was greatly reduced.

Chemical Effects

It has been found (Rafter, 1957) that unless special care is taken to ensure that all the SO_2 samples are prepared under exactly identical conditions, it is possible for errors of up to 3% in measured ratios to

occur. Thus it is necessary to ensure complete burning of the sulphur sample to sulphur dioxide as well as to ensure that burnings are performed at the same temperature. Several measurable differences found in preliminary work were later traced to this source.

Contamination of Sample

The chief contaminants of samples are air and CO_2 . The former results from the incomplete evacuation and degassing of the sample-filling system, and the latter from the presence of carbon in the sulphur from which the SO_2 is prepared. If any contaminating gas is present, the gas flows through the two leaks are not identical, and fractionation takes place. The most convenient way of checking for contamination is to compare the tube pressures for the sample and the standard for equal mass 64 voltages. Normally a sample is rejected if it contains more than 5% of any other gas.

Electronics

The accurate reading of isotope ratios demands stability of the associated electronic circuits, in particular the accelerating voltage and magnet current supplies. If either of these supplies varies, the ion beams move towards the edges of the slits and the peak heights begin to drop. As the two effective slit widths are not identical this causes the ratio to change also. The flat top of the ratio curve extends over a range of 1V in the accelerating voltage of 3,000V. Since the deflection of the ion beam in passing through the magnetic field is approximately proportional to i^2/V (where i is the magnet current and V is the accelerating voltage) this range of 1 in 3,000 in accelerating voltage is equivalent to a range of 1 part in 6,000 in the magnet current.

Any larger variation in either of these supplies causes a reduction in the accuracy of the result.

The source temperature also has an effect on the ratio. Any comparatively sudden changes in temperature such as those resulting from cold draughts cause the ratio to vary. It is hoped at some future date to temperature-control the source.

STANDARDS FOR COMPARISON

As there are many ways in which fractionation can take place in the mass spectrometer ion source and leaks, it is very difficult to obtain absolute ratios to any great accuracy. Measurements of the absolute isotopic ratio of sulphur have been made by Nier (1938) who estimated his results to be accurate to within 2%, and by Trofimov (1949) who obtained $^{32}\text{S}/^{34}\text{S} = 22.0 (\pm 1\%)$ for several samples of Meteoritic Sulphur. On the other hand by the use of techniques similar to those described in this paper it has been found possible to compare samples against a standard sample to an accuracy of 0.5‰ (see, for example, Thode *et al.*, 1954). This means that, in any laboratory the $^{32}\text{S}/^{34}\text{S}$ ratio

obtained depends on the $^{32}\text{S}/^{34}\text{S}$ ratio arbitrarily given to the standard used. If results from different laboratories in the world are to be compared it is necessary to be able to compare these standards. As one means of accomplishing this, the National Bureau of Standards, U.S.A. has made available Isotopic Reference Samples (Mohler, 1955) which can be compared with the standards used in each laboratory.

CHOICE OF NEW ZEALAND STANDARD

For the earlier work done in this laboratory, New Zealand sea water sulphate (collected at Titahi Bay) was used as the standard. As it was not possible at that time to compare this standard against overseas standards the $^{32}\text{S}/^{34}\text{S}$ ratio was taken as 21.77.

As a check on the repeatability of the results samples of cylinder SO_2 were compared against Sea Water Standards prepared on nine different days, spread over a period of two months and the results showed a standard deviation of 0.6‰. As this was not much greater than the standard deviation of most of the individual results, it was considered satisfactory. When later alterations to the mass spectrometer improved the standard deviation of individual readings to 0.2‰ for a good run, it became apparent from repeat runs on several samples that the standard samples prepared from this Sea Water Standard were not as constant in isotopic composition as had previously been thought.

After some consideration of available materials suitable to use as a working standard, Merck Sulphur was chosen and a 250-gram bottle of this was set aside specially for the purpose. This was used for a trial period during which it was compared occasionally with cylinder SO_2 and sea-water sulphate. It was found that the standard deviation of the measurements on the cylinder SO_2 and the sea-water sulphate was 0.2‰ in both cases. It was decided to continue to use Merck Sulphur as the working standard. This allowed a more straightforward chemical preparation (Rafter, 1957), and greater quantities of gas could be prepared at the one time. At the present time the standard deviation of a measurement as calculated from the recorder trace is 0.1 to 0.2‰ under the best conditions. However, this does not take into account variations caused by other errors both physical and chemical, and the results are usually given as having a standard deviation of 0.5 to 1‰.

COMPARISON WITH OVERSEAS STANDARDS

Recently the authors have compared the Merck Sulphur Standard with a sample of Pentlandite kindly supplied by Dr Jan Monster of McMaster University, Canada, and reported as having a $^{32}\text{S}/^{34}\text{S}$ ratio of 22.203 relative to a value of 22.225 assumed for Meteoritic Sulphur. The Merck Sulphur has also been compared with the N.B.S. Sulphur

Isotopic Reference sample No. 120 and with the New Zealand Sea-Water Standard. The results of these measurements are given in Table I. The first column of results gives the $\delta^{34}\text{S}$ values, taking Merck Sulphur as zero, and the last column gives the $^{32}\text{S}/^{34}\text{S}$ ratios calculated by taking Pentlandite as $^{32}\text{S}/^{34}\text{S} = 22.203$. These ratios thus conform to the scale used by Thode.

As a check on the δ scale of the Mass Spectrometer a sample of Cyrenaica Sulphur similar to that reported by Macnamara and Thode (1951) as having a $^{32}\text{S}/^{34}\text{S}$ ratio of 22.57 was also measured. The measurement obtained in this laboratory was $^{32}\text{S}/^{34}\text{S} = 22.55$. The agreement between these results is considered satisfactory.

TABLE 1.—Isotopic Composition of Various Sulphur Isotope Standards.

	$\delta^{34}\text{S}$ w.r.t. Merck (‰)	No. of Analyses	S.D. (‰)	$^{32}\text{S}/^{34}\text{S}$ and estimated error
Merck Sulphur	0.0	—	—	22.10 ± 0.01
Pentlandite	-4.4	4	0.2	22.203
N.B.S. (U.S.A.) Ref. Sulphur	-6.0	4	0.3	22.23 ± 0.02
Titahi Bay Sulphate ...	+13.0	5	0.2	21.82 ± 0.02

ACKNOWLEDGEMENTS

The authors wish to thank the following for supplying standard samples: Dr Mohler (N.B.S. Reference Standard), Dr Jan Monster (Pentlandite sub-standard), Mr I. Kaplan (Cyrenaica Sulphur). Miss J. Denman assisted with the mass spectrometer measurement of the samples.

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SULPHUR ISOTOPIC VARIATIONS IN NATURE

PART 5—SULPHUR ISOTOPIC VARIATIONS IN NEW ZEALAND GEOTHERMAL BORE WATERS

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(Received for publication, 13 January 1958)

Summary

The discharge from eleven geothermal bores at Wairakei has been examined for sulphur isotopic variations. It has been shown that the sulphide is 1.7% depleted in ^{34}S with respect to the sulphate. Assuming equilibrium conditions to exist at the site of the hot chloride water, from partition function calculations, the temperature corresponding to the equilibrium constant $K = 1.017 \pm 0.004$ calculated from sulphur isotopic measurements for the isotopic exchange reaction,



is $370 \pm 70^\circ\text{C}$. The highest temperature actually found for the hot chloride water that feeds the Wairakei bores is 270°C .

The average $\delta^{34}\text{S}$ value for eight bore discharges (-9.6%), is higher than reported for sulphur from magmatic steam (-17.5%). This discrepancy could partly be accounted for by loss of hydrogen sulphide since the formation of sulphate. Other geochemical evidence supports the hypothesis that gas has been lost from geothermal bore discharge.

INTRODUCTION

At Wairakei, one of the most important areas of hot spring activity in the geothermal region of New Zealand, drilling has been in progress for seven years. The object of drilling is to assess the geothermal power potential of the area, and to obtain steam for the power station now being erected. At the present time, 57 bores, varying in depth from 600 ft to 3,200 ft, have been drilled in the Wairakei area. The chemical investigation of the discharges of the bores is being carried out under the direction of one of the authors (S.H.W.). The bores, when drilling is completed, are allowed to discharge a mixture of steam and water containing roughly 30% by weight of steam. The sampling of this mixture presents some difficulties, and these have not yet been fully overcome. In planning the determination of the ratio of the sulphur isotopes in the bore discharges, consideration has to be given to the fact that the sulphur is present in two forms, as sulphate and as hydrogen sulphide, the latter being present in both the steam and water phases. As consideration must be given, both to the correct sampling of the discharge, and to the distribution of the sulphur, it

seemed desirable that the samples for isotope determination should be taken at the same time as a full sampling of the bore discharge was made. This was followed by the determination of the constituents of steam and water, as the main part of the chemical investigation.

Samples of water and condensate from eleven bores were collected for sulphur isotope investigations. From the analytical data and the steam-water ratio of the discharges at the time of collection, the average $^{32}\text{S}/^{34}\text{S}$ isotopic ratio for these discharges has been calculated, and is reported in Table 6.

This paper should be regarded as a preliminary investigation as to the type of information that a study of sulphur isotope ratios in geothermal discharges is likely to give, rather than as a complete survey of the area.

METHOD OF COLLECTION

Sampling of Bore Discharge

As the ratio of steam to water in the discharge is about 30 to 70 by weight, but 700 to 1 by volume, it is quite impossible to sample the discharge as a whole. It is necessary to separate steam from water, and sample each separately. A portion of the discharge is taken from a 1-in. valve in the discharge pipe of the bore, and led through insulated piping into a small cyclone separator discharging the separated steam and water into the air.

It is now well established that, in general, the steam in the discharge is produced by flashing from hot water tapped by the bore. Any gas in the steam was originally in solution in this water. In other words, underground there is only one phase—liquid water. The rational way of expressing the analytical results is to give the composition of this water phase.

To do this, it is necessary to know the steam-water ratio of the discharge, or the enthalpy of the discharge. It would have been desirable to have made this determination at the time of sampling, but unfortunately there was then no simple method that the chemist could use and it has been necessary to rely on measurements made by Ministry of Works engineers. These measurements may have been taken a long time before the sampling. However, it appears that the outputs of the bores remain fairly constant in quality, and although in theory, if there is only one phase below, the quality should not vary with the well-head pressure, in practice, the steam-water ratio does depend somewhat on the pressure. The Ministry of Works supplies graphs showing the variation of the outputs of steam and water with the well-head pressure. From these graphs, if the well-head pressure is taken at the time of sampling, it is possible to obtain the steam-water ratio.

There are some advantages in using a separator discharging into the atmosphere. It does not need to withstand pressure and can be

fairly light. A large amount of steam and water can be passed through it, so that any corrosion effects are negligible. Also, if there is any error in the enthalpy of the discharge, the error in the calculated composition of the underground liquid phase is least if the samples are taken at atmospheric pressure. Unfortunately, if the portion of the discharge taken into the separator does not contain steam and water in the proportions in which they occur in the discharge, there are errors in the contents of the constituents as calculated from the analyses of the water and steam. These errors are due to the fact that if excess steam or excess water is taken at pressures higher than atmospheric, then the heat given up by this excess in cooling to 99°C (the boiling point at Wairakei) goes to evaporate more steam from the water. The error due to this cause is not large if the sampling valve is near the point of discharge to the atmosphere. In the last few years, the only sampling points available have been valves provided before and after the orifice discs put in some distance before the silencer on the end of the pipe. These valves are used for the pressure readings to keep a check on the output of the bore. On the smaller bores the pressures at these points were not very high (≈ 50 lb per sq. in. gauge (p.s.i.g.)), but on recent production bores, the pressures have become very high, as much as 200 p.s.i.g. Sampling errors at these pressures may be large, and there may also be large errors at moderate pressures if water or steam is taken in large excess. Hence, it is the practice to measure the steam-to-water ratio in the portion of the discharge taken through the separator, and this was done with all but one of the samplings made for sulphur isotope ratio investigation. It is necessary again to know the enthalpy of the bore discharge, and from this, the factors can be calculated to correct the analyses of steam and water.

The water in the discharge is not uniformly dispersed within the steam, but travels along the wall of the pipe more slowly than the steam. Recent work has indicated that the water at high pressure may not be in equilibrium with the steam at any point and this may cause an error of up to 15% in, for instance, the chloride content. This difficulty in sampling has not yet been overcome, and it is possible that these preliminary results for the sulphur isotopes in the whole discharge will require modification later.

Water Samples

FOR CHEMICAL ANALYSIS

The water sample bottles were of 500 ml capacity and were sealed by butyl rubber tubing 16 cm long and 2.4 cm inside diameter. The bottles were filled by a stream of water from a tube connected to the water-outlet pipe of the separator so that they were well purged of any water affected by air. The rubber tube was then closed with a screw clip.

In the Wairakei laboratory, one bottle of water was used to determine, as soon as possible after collection, the hydrogen sulphide content of the water, by titration of a sample with 0.02 N iodine solution. Another sample bottle was taken to the Dominion Laboratory in Wellington for chemical analysis. After a determination of carbon dioxide on a portion, hydrogen sulphide was removed from the remainder by a current of nitrogen. Sulphate was then determined on a sample passed through an ion exchange column, by titration with barium perchlorate with thorin as indicator according to the method of Fritz and Yamamura (1955).

FOR SULPHUR ISOTOPE DETERMINATIONS

For the first four bores sampled, 18, 24, 8A, and 14, a sample for both sulphate and hydrogen sulphide in solution was collected in a 2½-litre bottle. However, hydrogen sulphide is readily lost even from a large bottle, and no sulphide could be recovered from these samples. It was therefore decided to collect separate samples for sulphate and sulphide. For the remaining bores about 5 litres of water were collected in a plastic bucket, some glacial acetic acid added and a current of nitrogen passed through at once to remove hydrogen sulphide. A 2½-litre bottle was then filled with the water for sulphate estimation. Acetic acid was chosen as a convenient acid to add as the amount necessary would not be critical and it was safer to transport in the field than concentrated hydrochloric acid. Its use seems to have been unfortunate as its presence encouraged bacterial growth. Moreover, it appeared from later work that when hot water containing hydrogen sulphide was exposed to air, the oxidation of hydrogen sulphide was very rapid. Hence the sulphur formed by oxidation of hydrogen sulphide would be present in the water, and it would not be possible later to distinguish this from any sulphur formed by bacterial reduction of sulphate.

Hydrogen sulphide in solution in the water, partly as hydrosulphide ion, and partly as free hydrogen sulphide, amounts to an appreciable proportion of the total hydrogen sulphide. It was hoped to obtain a sample of this by adding silver nitrate to a sample of water in the plastic bucket. A black precipitate was obtained, and this was allowed to settle, the water decanted off, and the precipitate washed into a sample bottle. It appeared, as mentioned above, that hydrogen sulphide was oxidised very rapidly when the hot water was exposed to the air. The sulphur formed would be in such fine suspension that it would be poured away with the water.

Gas Sample

The main difficulty in the collection of gas samples from the separated steam was the very small content of gas in the steam, so that a very large amount of condensate was collected for a small

amount of gas. On account of the solubility of hydrogen sulphide in water, both condensate and gas had to be collected together. The method adopted was to draw a sample of steam into a 10-litre flask. The steam was taken from the steam outlet of the separator by means of a stainless steel tube inserted into the pipe. Air was removed from the flask by first forcing water from a trap up into the steam. The pump was then reversed so that the flask was purged with steam. A rubber tube connecting the flask to the pump was closed by a screw clip. Steam and gas were drawn into the flask in a steady flow by cooling the flask with cold water. The process was speeded up by inserting a condenser between the flask and the inlet. Collection was complete when the flask no longer heated up on removing the cooling water. The flask was then closed by a screw clip on the butyl rubber connecting tube. Back at the field laboratory, about 160 ml of 20% NaOH solution was added to the flask to transfer all the carbon dioxide and hydrogen sulphide to the condensate phase. The residual gas was pumped off. The volume of condensate was measured, and a portion kept for analysis. Hydrogen sulphide was determined in the alkaline condensate by adding enough 40% NaOH to a sample to bring the concentration of NaOH to 20%, and then titrating with 0.1 N iodine, the end-point being detected by potentiometric titration using the dead stop end-point.

For sulphur isotope ratio determination, a 2½-litre bottle filled with the alkaline condensate was taken.

CHEMICAL PROCEDURE FOR SULPHUR ISOTOPE EXAMINATION

On receipt of the specimens it was not possible to examine them immediately. It was first thought that the waters and condensates would contain simply sulphate and sulphide, and methods were developed to remove these quantitatively for sulphur isotopic examination. In some cases, nickel sulphide was present in the condensates so that the bottles had to be well shaken before taking a suitable aliquot.

Water Phase

For the recovery of sulphide, from those waters not previously tested as above 2 litres of water were placed in the extraction column shown in Fig. 1. The water was acidified by the addition of 1.1 HCl and nitrogen bubbled through the column for 1 hr. Any sulphide-sulphur present was collected in the silver nitrate bubblers. After removal of sulphide, the water was transferred to a 2-litre beaker and evaporated down to 100 ml. If silica precipitated at this stage, the solution was neutralised by the addition of several drops of 20% NaOH, re-acidified with HCl, transferred to a 100 ml platinum basin and the silica dehydrated on the water-bath and removed by filtration. From the filtrate, sulphate was precipitated with BaCl₂ in the usual way. The sulphate, after ignition and weighing to obtain the weight of

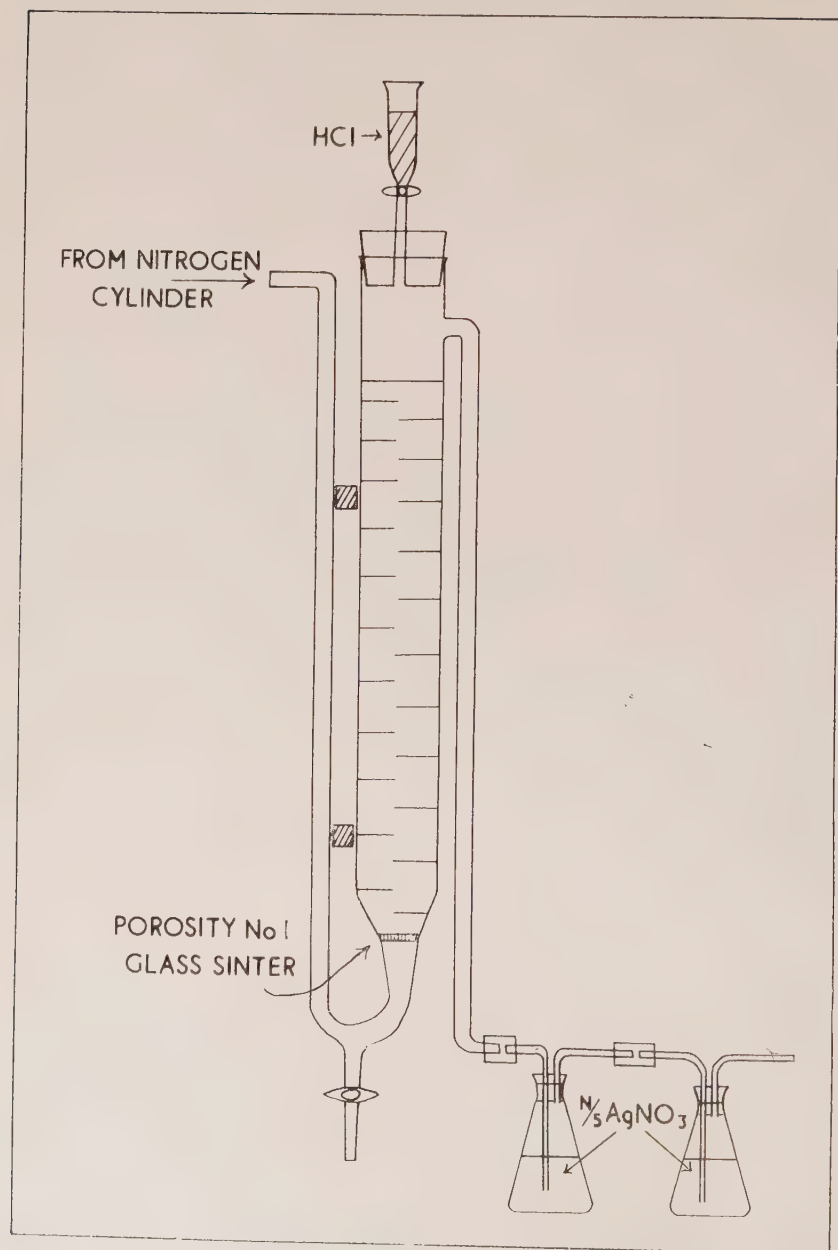


FIG. 1.—Extraction column used for recovery of sulphide-sulphur.

sulphate-sulphur, was reduced with carbon to barium sulphide and the sulphide recovered as silver sulphide for the preparation of sulphur dioxide gas for mass spectrometer examination, as described by Rafter (1957).

The residues recovered on the addition of AgNO_3 to the bore waters at Wairakei were mainly silver chloride. This was removed by solution in 1:4 NH_4OH . These black residues, as well as any black residues recovered by sweeping bore-water with nitrogen, either at the bore site or in the laboratory, were examined to identify the presence of sulphide by burning in a stream of oxygen in a tube furnace. Any sulphur dioxide evolved was bubbled through water coloured by several drops of N/10-iodine solution. If the iodine titre indicated the presence of several milligrams of sulphide-sulphur, the sulphate was recovered for isotopic examination.

It appeared that the black residues recovered from bore-waters were not Ag_2S , as there was in every case only a trace of sulphide-sulphur in these residues.

Gas Phase

The condensates were examined for sulphide-sulphur using a $\frac{1}{2}$ -litre extraction column and a 100 to 500 ml aliquot. An additional AgNO_3 bubbler was added to the train. After acidification and the removal of sulphide, the solution was examined for sulphate. It was soon observed that the milligrams of sulphur recovered as sulphide and sulphate did not always quantitatively agree with the milligrams of sulphur recovered as total sulphur obtained by oxidation of water or condensate with bromine. This indicated the existence of an additional form of sulphur, the most likely assumption being the presence of colloidal sulphur.

To recover this form of sulphur it was necessary to burn the barium sulphate precipitates in oxygen (after drying in an air oven) in a tube furnace, passing the exit gases through iodine solution. This procedure detected and recovered any sulphur in the barium sulphate. From the iodine solution this sulphur could be precipitated and recovered as sulphate.

The filtrate after the removal of the main barium sulphate precipitate was usually perfectly clear, but on the addition of bromine a heavy precipitate of barium sulphate frequently resulted.

This additional form of sulphur cannot be sulphite-sulphur as any sulphite would have been eliminated on acid digestion. It could be a polythionate that precipitates sulphur on acidification and forms thiosulphate. The solubility of barium polythionate could account for the clear filtrate precipitating sulphate on bromine oxidation.

The exact form of this sulphur has not been identified. For the purposes of this paper, the sulphur recovered from the burning of the barium sulphate precipitates and from the filtrate remaining after the removal of sulphate, is reported as sulphur-sulphur.

MASS SPECTROMETER MEASUREMENTS

All mass spectrometer measurements reported in this paper have been made in accordance with the procedures reported by Hulston and Shilton (1958). The sulphur isotopic ratios in the samples have been measured with respect to sea-water sulphate as standard and the results expressed as $\delta^{34}\text{S}$ values in parts per thousand (‰) using the formula

$$\delta^{34}\text{S} = \frac{{}^{34}\text{S}/{}^{32}\text{S} (\text{samples}) - {}^{34}\text{S}/{}^{32}\text{S} (\text{standard}) \times 1,000/1}{{}^{34}\text{S}/{}^{32}\text{S} \text{ standard}}$$

In Table 6, the sulphur isotopes have also been reported as ${}^{32}\text{S}/{}^{34}\text{S}$ ratios assuming a value of 21.77 for the ${}^{32}\text{S}/{}^{34}\text{S}$ ratio in sea-water sulphate.

RESULTS

Changes in Samples on Storage

WATER PHASE

Table 1 (column A) shows the milligrams of sulphur as sulphate-sulphur recovered per litre from eleven bores at Wairakei, and the ${}^{34}\text{S}/{}^{32}\text{S}$ sulphur isotopic enrichment ratio ($\delta^{34}\text{S}$) with respect to the sea-water sulphate standard expressed in parts per thousand (‰). The average $\delta^{34}\text{S}$ value $+2.1\text{‰}$ indicates that the bore-water sulphate is slightly depleted in the lighter isotope with respect to sea-water sulphate. In no case could sulphide be detected in the water phase. However, from the sulphide precipitated at Wairakei as Ag_2S in the water phase, by the combination of the small residues from Bores 21, 16/1, and 16 (R59, 60, and 61), sufficient sample was obtained for an isotopic examination. The $\delta^{34}\text{S}$ value given in the foot-note to Table 1 showed that this sulphide had the same isotopic ratio as the sulphide-sulphur in the gas phase.

When the samples were examined several months later, they were found to contain, in most cases, less sulphate-sulphur, as shown in column B. The average $\delta^{34}\text{S}$ value $+0.9\text{‰}$ showed a slight enrichment in the $\delta^{32}\text{S}$ isotope with respect to the first measurement. The discrepancy in the sulphate-sulphur could be accounted for as sulphur-sulphur (S-S) as explained above, and shown in column C. As much as 28% of the original sulphate-sulphur now existed as sulphur-sulphur. The weight of sulphur recovered as sulphur-sulphur was unfortunately too small for mass spectrometer examination, except in two samples where the average $\delta^{34}\text{S}$ value $+1.5\text{‰}$ indicated that this sulphur was not sulphide-sulphur oxidised to sulphur, as can be seen from the condensate sulphide-sulphur $\delta^{34}\text{S}$ values given in Table 2, and for the one combined-sulphide recovered from bore-waters. Of

TABLE 1.—Sulphur in Bore Discharge-Water Phase.

Sample No. (R. series)	Bore No.	A		B		C		D	
		Sulphate-sulphur (mg/l)	$\delta^{34}\text{S}$ (‰)	Sulphate-sulphur (mg/l)	$\delta^{34}\text{S}$ (‰)	Sulphur-sulphur (mg/l)	% of Sulphate-sulphur A.	Total S (mg/l)	$\delta^{34}\text{S}$ (‰)
28	8A	13.2	-1.1						
29	14	10.5	+5.0	10.4		1.1	10.4	10.6	+0.9
30	18	9.3	+5.3						
31	24	12.5	+1.8	9.3		1.5	14.0	10.8	-1.3
58	12	9.1	+3.2	9.8	+0.7	0.8	8.8	14.3	+1.2
59	21	10.2	+5.9	9.0	+2.5	1.9	18.6	10.9	+1.9
60	16/1	10.0	+2.2	8.6	-0.1	2.7	27.0	10.4	+2.1
61	16	8.2	-0.6	6.2	-1.3	1.6	19.5		
71	1	11.5	+1.3	9.5	+3.2	1.7	14.7		
72	11	11.1	-0.1	7.6	-0.9	3.1	27.9		
73	13	13.5	-0.7	11.3	+2.6	2.0	14.8		
			Av. +2.1		Av. +0.9				Av. +1.0

NOTE. The combined sulphide-sulphur recovered from the water-phase for bores 21, 16/1, and 16 was negligible, but sufficient was available for an isotopic measurement giving a $\delta^{34}\text{S}$ of $-13.5 \pm 0.7\%$.

the sulphur-sulphur, approximately 80% was recovered from the combustion of the barium sulphate precipitate, 20% from the filtrate after removal of barium sulphate. In column D, where sufficient sample was available, total sulphur was estimated and the average $\delta^{34}\text{S}$ value $+1.0\text{‰}$ indicates that the sulphur isotopic ratio for the water phase of the bore discharge does not differ significantly from that of the sea-water standard.

GAS PHASE

The milligrams of sulphur per litre for various forms of sulphur collected in the gas phase are recorded in Table 2, together with the $\delta^{34}\text{S}$ values.

The results in Table 2 bring out some interesting facts. When Bore 8A was first examined both sulphide and sulphate were present. A second bottle of condensate from the same bore had a precipitate of nickel sulphide present but nearly four times as much sulphate-sulphur. On re-examining the condensate two months later, no sulphide was present, the sulphate had decreased slightly but 17 mg of sulphur-sulphur were recovered. Total sulphur recovered by bromine oxidation of the condensate is shown in column D. An examination of the $\delta^{34}\text{S}$ values showed that significant errors can occur if only sulphide-sulphur was accounted for. It was evident that while in the water-phase sulphate was capable of reduction to sulphur-sulphur, in the gas phase the sulphide in the condensate was being oxidised to sulphur-sulphur and sulphate.

The results for Bore 14 confirmed these conclusions. When the condensate was first examined no sulphate could be detected. When re-examined six days later, an amount of sulphate equivalent to the sulphide present was recovered. As sulphur-sulphur had not been looked for on the first examination, it may be concluded that this sulphur had oxidised to sulphate. On analysing the remainder of the condensate three months later, there was no sulphide present but now more sulphur-sulphur than sulphate-sulphur. Whereas in the water-phase sulphur-sulphur, 80% of it was recovered during the burning of the BaSO_4 precipitate, from the gas-phase sulphur-sulphur, for the cases examined, 70 to 80% was recovered from the filtrate after BaSO_4 precipitation. The reason for this reversal needs further investigation.

The necessity for either very carefully examining bore discharges for the various forms of sulphur in order to get the overall average for the sulphur or for completely oxidising all forms of sulphur by the addition of bromine, both to the water-phase sulphur and gas-phase sulphur, was apparent from these analyses. Another alternative would be to sterilise the samples to avoid the bacterial action suspected in the samples after collection.

The remaining condensates shown in Table 2 were examined for total sulphur only.

The average $\delta^{34}\text{S}$ values — 15.9‰, for these bore condensates showed conclusively that the $^{34}\text{S}/^{32}\text{S}$ isotopic ratio for the sulphide-sulphur in the gas-phase of the discharge for the bores examined, was greatly enriched (1.7%) in the lighter isotope of sulphur in comparison with the sulphate-sulphur issuing at the same time in the water phase.

Sulphur Isotopic Ratio on the Whole Discharge

To assess the true sulphur isotopic ratio for the geothermal bores in the Wairakei area, it was necessary to know the steam-water ratio for each bore and the gas content of the steam.

From the total sulphur content of the condensates (Table 2) the content of the hydrogen sulphide in the steam has been calculated and shown in Table 3, column 4. There is a further correction of about 1% to be added to these values for the volume of sodium hydroxide solution added to the condensate in the gas collection flask. From the content of gas in the steam, determined by one of the authors (S. H. W.), the hydrogen sulphide content of the gas can be calculated.

These results given in Table 3 are of interest in comparing the H_2S content of various bores. The various $\delta^{34}\text{S}$ values for sulphide given in Table 2 have been re-tabulated in Table 3, column 9.

There is a small amount of hydrogen sulphide in solution in the water phase. Although there was not enough of this in the samples to recover for the determination of the sulphur isotopic ratio, the content had been determined chemically on a separate sample soon after collection. From the steam-water ratio in the bore discharges at atmospheric pressure, as calculated from the data for the enthalpies of the bore discharges obtained from the Ministry of Works' engineers, the content of hydrogen sulphide in the water phase has been calculated on the whole discharge as shown in Table 4.

To obtain the total hydrogen sulphide on discharge, to the values obtained in column 6, Table 4, must be added the hydrogen sulphide in the steam phase, similarly expressed. The total hydrogen sulphide on discharge is given in column 10, Table 4.

As seen from Table 4, the hydrogen sulphide in solution in the water (as free hydrogen sulphide and as hydro-sulphide ion, HS^-) can amount to a considerable proportion of the total hydrogen sulphide (5 to 50%).

In Table 5, the content of sulphur in the form of sulphate in the water as found in the chemical analysis, is expressed in a similar way as a content in the whole discharge.

From the content of sulphide-sulphur and sulphate-sulphur in the discharge of the bores, and the average $\delta^{34}\text{S}$ values for sulphur in sulphide and sulphate forms from each bore, the average value $\delta^{34}\text{S}$ for the discharge of the various bores has been calculated and set out in Table 6.

TABLE 3.—Percentage of Sulphur in the Gas as Hydrogen Sulphide.

Sample No. (R. series)	Bore No.	Total sulphur (mg/l)	H ₂ S (milli- mole per 100 mole of condensate)	Correction factor	True H ₂ S content of steam (milli- mole per 100 mole of condensate)	Gas content of steam (%)	H ₂ S content of gas (%)	$\delta^{34}\text{S}$ (‰)
71	1	68.0	3.82	1.11	4.24	0.20	2.14	-14.4
72	11	29.7	1.67	0.715	1.19	0.027	4.42	-17.4
59	21	80.3	4.51	0.76	3.42	0.105	3.19	-18.4
61	16	22.9	1.29	0.726	0.935	0.032	2.94	
60	16/1	4.2	0.235	0.929	0.22	0.016	1.36	
30	18	54.0	3.03	1.400	4.25	0.124	3.43	-12.6 } -12.5 }
28	8A	42.8	2.40	1.25	3.01	0.133	2.27	-15.3 } -15.6 }
29	14	82.8	4.65	0.915	4.26	0.147	2.90	-12.8 } -15.3 }
31	24	24.3	1.32	1.15	1.515	0.056	2.72	
58	12	8.1	0.455	1.10	0.500	0.029	1.71	-19.4
73	13	9.5	0.535	1.09	0.58	0.010	5.9	-16.4

TABLE 5.—Sulphate in Total Discharge.

Sample No. (R. series)	Bore No.	Sulphate in water (p.p.m.)	Correction factor	Sulphate in water (millimole per 100 mole of water)	Content of water in discharge at atmos. press. (%)	Total sulphate in water (millimole per 100 mole of discharge)	$\delta^{34}\text{S}$ (‰)
71	1	32.5	0.90	0.55	62.0	0.34	+1.3 +3.2
72	11	33	0.97	0.73	74.4	0.54	-0.1 -0.9
59	21	32.5	0.975	0.60	72.2	0.43	+5.9 +2.5 +1.9
51	16	26.5	0.98	0.485	74.2	0.36	-0.6 -1.3
60	16/1	30.0	0.99	0.56	67.9	0.38	+2.2 -0.1 +2.1
30	18	34.0	1.01	0.65	78.7	0.51	+5.3
28	8A	41.0	1.01	0.78	56.6	0.44	-1.1
29	14	41.0	0.98	0.75	59.6	0.45	+5.0 +0.9
31	24	37.5	1.004	0.705	65.4	0.46	+1.8 -1.3
58	12	33.0	0.985	0.61	82.2	0.50	+3.2 +0.7 +1.2
73	13	38.5	0.975	0.70	82.15	0.58	-0.7 +2.6

TABLE 6.—Average Sulphur Isotopic Ratio for Geothermal Bore Discharge.

Description	Sam- ple No. (R. ser.)	Bore No.	Total H ₂ S in discharge (millimole per 100 mole) (a)	Sulphide average $\delta_{34}\text{S}$ (‰)	Total SO ₂ in water (millimole per 100 mole) (b)	Sulphate average $\delta_{34}\text{S}$ (‰)	Total sulphur (millimole per 100 mole in discharge) (a + b)	Average $\delta_{34}\text{S}$ $\frac{a\delta_1 + b\delta_2}{a + b}$ (‰)	$^{32}\text{S}/^{34}\text{S}$ ratio
Bores producing from per- meable volcanics	71	1	1.70	-14.4	0.34	+2.25	2.04	-11.6	22.02
	72	11	0.43	-17.4	0.54	-0.5	0.97	-8.0	21.94
	59	21	1.05	-18.4	0.43	+3.4	1.48	-12.0	22.03
	61	16	0.32	-(16.0)	0.36	-0.95	0.68	-8.1	21.95
	60	16/1	0.15	-(16.0)	0.38	+1.4	0.53	-3.5	21.85
	30	18	0.96	-12.55	0.51	+5.3	1.47	-6.4	21.91
Bores producing from per- meable volcanics just un- der impermeable lake silt- stone, excess steam	28	8A	1.38	-15.45	0.44	-1.1	1.82	-12.0	22.03
	29	14	1.80	-14.05	0.45	+2.95	2.25	-10.61	22.00
Bore producing from fissure in ignimbrite	31	24	0.61	-(16.0)	0.46	+0.25	1.07	-8.1	21.95
Bores near Karapiti, dis- charge of low enthalpy	58	12	0.18	-19.4	0.59	+1.7	0.68	-3.9	21.85
	73	13	0.20	-16.6	0.58	+0.95	0.78	-3.5	21.85
				Av. -15.6±2*		Av. +1.4±2*		Av. -9.6±2†	21.98±0.04

*Neglecting Bores 12 and 13 in these averages

†Neglecting Bores 16/1, 12, and 13 in this average

DISCUSSION

Bacterial Oxidation and Reduction after the Collection of Samples

Bigeleisen (1949) has shown that isotopic molecules have different reaction rates and that, in general, the molecule containing the lighter isotope reacts faster. He has derived a formula giving the approximate ratio of the rate constants for competitive reactions of isotopic molecules. The isotopic compounds of sulphur differ in their chemical properties and fractionation of the isotopes will occur in equilibrium and unidirectional processes.

It is shown in Table 2 that condensate sulphide is oxidised to soluble sulphur-sulphur and sulphate. This may be considered as a unidirectional process and, applying Bigeleisen's principle, the sulphate formed should be enriched in the lighter sulphur isotope. The lower $\delta^{34}\text{S}$ values for sulphate support this possibility. Another possibility is that the oxidation of sulphide to sulphate is biological.

While the oxidation of sulphide to sulphur is understandable, the further oxidation of condensate sulphide to sulphate is difficult to explain chemically. The reduction of bore-water sulphate to sulphur is more difficult chemically, so it would seem that bacterial oxidations and reductions were responsible for the oxidation of condensate sulphide to sulphate (Table 2) and the reduction of water sulphate to sulphur-sulphur (Table 1), that occurred in the samples after collection.

The $\delta^{34}\text{S}$ values for water phase sulphate-sulphur and gas phase sulphide-sulphur obtained from the sulphur recovered as total sulphur in each phase, represent the true isotopic values for the sulphur in each phase at the time of collections. These values have been used in Tables 3 to 6 to obtain the average sulphur isotopic value for bore discharge.

Fractionation of the Sulphur Isotopes

From Table 6, the average $\delta^{34}\text{S}$ value for bore-discharge sulphate is $+1.4\%$, and for the H_2S is -15.6% . If the sulphate is formed from hydrogen sulphide by inorganic oxidation, the fractionation of the sulphur isotopes is in accordance with the isotopic exchange reaction,



if it is assumed that equilibrium conditions exist in the bore discharge. Tudge and Thode (1950) were the first to make extensive use of the thermodynamic properties of isotopic compounds of sulphur to calculate partition function ratios. From such ratios the equilibrium constants of isotopic exchange reactions such as given in equation (1) can be obtained. The equilibrium constants at 0°C and 25°C for the above exchange reaction are given as 1.085 and 1.074 respectively.

The equilibrium constant can be calculated from the enrichment factors (δ) obtained for the sulphur isotopes as sulphate in the water phase ($+1.4\%$) and as sulphide in the gas phase (-15.6%), reported in Table 6. From this data the equilibrium constant for reaction (1) is

$$K = \frac{1 + \delta^{34}\text{SO}_4}{1 + \delta^{34}\text{S}}$$

$$= \frac{1.0014}{0.984}$$

$$= 1.017_6$$

Since partition function ratios are temperature dependent, this isotopic equilibrium constant may be used to determine the temperature at which the equilibrium represented by equation (1) was established.

Partition function ratios were calculated for H_2S and $\text{SO}_4=$ at 0, 100, 200, 300, and 500°C . Equilibrium constants were then found by dividing the $\text{SO}_4=$ partition function ratio at these temperatures by the H_2S partition function ratio. The results are shown in Table 7 and plotted on the graph in Fig. 2. The results reported in Table 7 agree well with partition function ratios recently published by Sakai (1957). The equilibrium constants are greater than unity, indicating that ^{34}S becomes concentrated in the $\text{SO}_4=$. From the graph, the temperature corresponding to $K = 1.017$ is 360°C . Taking into consideration the standard deviations quoted in Table 6, the value for K lies between 1.021 and 1.013, so that the equilibrium temperature should best be quoted as $370 \pm 70^\circ\text{C}$. The calculated temperature of water at depth to give the mean steam content of the bore discharge as actually found is 255°C , (Ellis and Wilson, 1955). The highest temperature actually found was 270°C in Bore 25, at depth 2,230 ft.

If the sulphate in the water phase has been formed by oxidation of steam phase H_2S in a unidirectional reaction, the ^{34}S isotope should be more abundant in the water-sulphate than in the H_2S . The fact that the water-sulphate is enriched in the ^{34}S isotope points to the fact that either its origin is entirely different from that of the steam phase H_2S or that in the geothermal bore discharge, an isotopic equilibrium does exist. Support for this possibility would be the known strongly reducing gases, particularly hydrogen, present in these gases. The presence of hydrogen would enable isotopic equilibrium to be established.

This could mean that the temperature calculated from the isotopic equilibrium constant, $370 \pm 70^\circ\text{C}$, does in fact represent a temperature

TABLE 7.—Partition-functions ratios for $\text{H}_2^{34}\text{S}/\text{H}_2^{32}\text{S}$ and $^{34}\text{SO}_4=^{32}\text{SO}_4=$ at Various Temperatures and the Associated Equilibrium Constant.

Temperature (°C)	$\text{H}_2^{34}\text{S}/\text{H}_2^{32}\text{S}$	$^{34}\text{SO}_4=^{32}\text{SO}_4=$	K
0	1.011 0	1.096 6	1.084
100	1.010 0	1.060 3	1.050
200	1.007 2	1.040 2	1.033
300	1.005 5	1.028 2	1.022
500	1.003 4	1.016 2	1.013

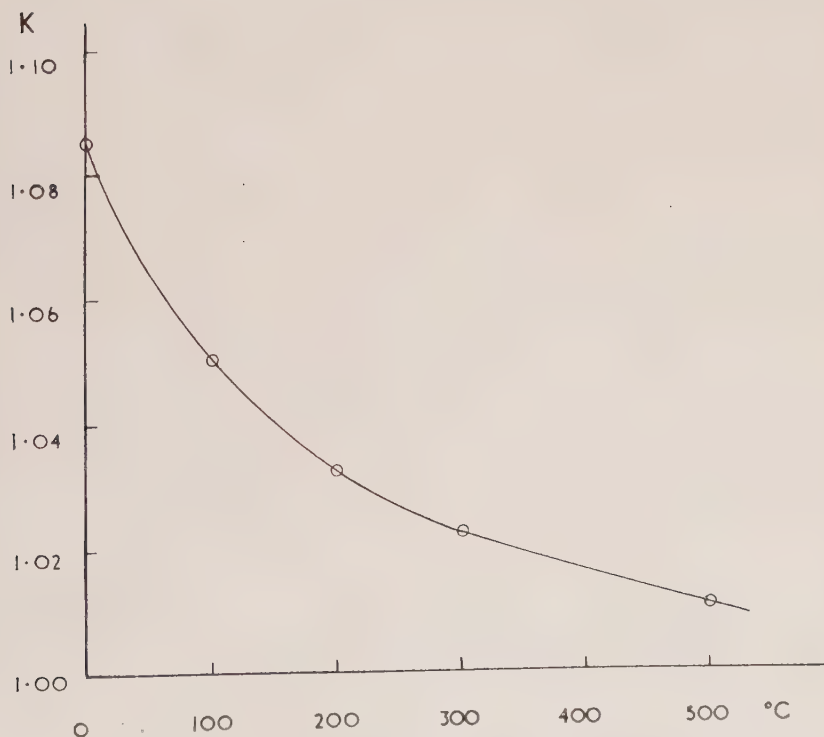


FIG. 2.—Graph showing the variation of the sulphide-sulphate isotopic equilibrium constant (K) with temperature (°C).

of the right order existing underground at the site where the equilibrium was established.

Loss of Sulphide-Sulphur in the Bore Discharge

The millimoles of sulphate-sulphur in discharge per 100 moles H_2O , as shown in Table 6, are remarkably constant. On the other hand, the millimoles of sulphide-sulphur vary by as much as a factor of twelve. Both this fact and the large variation in the gas content of total discharge (Table 3, column 7) indicate that there has been considerable loss of gas from the underground chloride water.

Owing to this loss of gas, it is not possible to deduce accurately the true sulphur isotope ratio of the parent material underlying the geothermal region. The values for $\delta^{34}\text{S}$ for total sulphur in the bore discharges are given in the second to last column of Table 6. There is considerable variation in these $\delta^{34}\text{S}$ values. Neglecting the $\delta^{34}\text{S}$ values of the whole discharge for Bores 16/1, 12, and 13, which have very low content of gas in the steam, the average $\delta^{34}\text{S}$ value for total sulphur in discharge is $-9.6 \pm 2\%$. This corresponds to a $^{32}\text{S}/^{34}\text{S}$ ratio of 21.98 ± 0.04 . From investigations on White Island fumaroles (Rafter *et al.*, 1958), it has been found that the sulphur isotopic ratio for sulphur in magmatic steam is about 22.15, that is a $\delta^{34}\text{S}$ value of -17.5% . As it would appear that there has been a loss of hydrogen sulphide gas from the hot chloride water, this loss could partly explain the difference between White Island magmatic sulphur ($\delta^{34}\text{S} - 17.5\%$) and bore discharge at Wairakei ($\delta^{34}\text{S} - 9.6\%$), but further discussion of the problem from other geochemical evidence is required.

It seems probable that the sulphur in the bore discharges is derived from magmatic steam. At high temperatures the sulphur would be in the steam partly in the form of sulphur dioxide and sulphur, as well as H_2S . As the temperature falls, reaction with hydrogen (which is also a constituent of magmatic steam) would take place, with the formation of hydrogen sulphide. The geothermal chloride water tapped by boring at Wairakei is formed by the mixing of magmatic steam with ground water. It seems likely that the origin of this ground water is Lake Taupo. If all the heat is supplied by magmatic steam, the content of magmatic steam in the underground chloride water would be about 25%, but this seems on general grounds to be rather high, Wilson (1955). A likely hypothesis is that the sulphate in this underground chloride water is due to the oxidation of hydrogen sulphide by atmospheric oxygen dissolved in the ground water. The content of sulphate in the bore discharges is about 23 p.p.m. and this is approximately double the amount that could be formed by oxygen in ground water, assuming 90% of ground water in the mixture, with water of magmatic origin. The water of Lake Taupo has been found to contain 8 p.p.m. of sulphate, and as this sulphate is probably derived from volcanic activity in Tongariro National Park, the amount of sulphate may be lower in water when the volcanoes are not so active as they

have been recently. However, even a content of 8 p.p.m. is not enough to account for all the sulphate found. It is possible that some of the sulphate could be due to the oxidation of hydrogen sulphide in surface springs, or of sulphur deposited at the surface from geothermal steam, but there is no evidence that the ground water in the underground chloride water has come from surface water near the active area where it could have picked up this sulphate. It is more likely that some of the sulphate in the underground chloride water is formed by the oxidation of hydrogen sulphide by ferric compounds in the rocks permeated by the hot acid water. Iron sulphide could not form on account of the acidity. At Wairakei, there is not much sulphate to account for in the water, but at Waiotapu, for instance, the sulphate content of the underground chloride water is about 70 p.p.m.

It appears probable, therefore, that most of the sulphate in the hot chloride water has been formed by oxidation of hydrogen sulphide, which was originally associated in the magmatic steam with the hydrogen sulphide still remaining in the chloride water.

There still remains, however, the problem of whether loss of hydrogen sulphide could explain the differences in the average $\delta^{34}\text{S}$ value for Wairakei and White Island sulphur. This can best be illustrated by an example. The average sulphate content of the chloride water is from the results for eight bores 0.44 millimole per 100 mole of water, and the hydrogen sulphide content is 1.03 millimole. With the $\delta^{34}\text{S}$ value for the sulphate $+1.4\%$ and for the sulphide -15.6% the average $\delta^{34}\text{S}$ value is -9.6% . If there has been a 90% loss of H_2S , then originally there would have been 10.3 millimole of H_2S . The average $\delta^{34}\text{S}$ value under these conditions would be -14.8% . This result is much closer to the present-day average for White Island sulphur (-17.5%), but even if the ratio of H_2S to sulphate was very much greater $\delta^{34}\text{S}$ could not exceed an average value of -15.6% .

There is, however, the discrepancy, that the $\delta^{34}\text{S}$ value (-15.6%) for hydrogen sulphide in the bore discharge is slightly higher than that for sulphur in magmatic steam at White Island (-17.5%). If the sulphate has come from hydrogen sulphide originally associated with it in the magma, then isotopically, as the sulphate is enriched in $\delta^{34}\text{S}$, the sulphur in the hydrogen sulphide should be depleted. Thus, if sulphur in the hot chloride water was isotopically the same as that at present in the magmatic steam at White Island, with a $\delta^{34}\text{S}$ of -17.5% , the sulphur in the hydrogen sulphide of the bore discharges should show a $\delta^{34}\text{S}$ value lower than -17.5% .

Four possible explanations for this discrepancy must be considered:

- (1) That the sulphate was originally not associated with the hydrogen sulphide in the underground chloride water, has been rejected above.
- (2) That an actual decrease may be obscured by experimental errors, especially in the determination of the $\delta^{34}\text{S}$ value for sulphur at White Island, for this has had to be calculated

from the $\delta^{34}\text{S}$ values for sulphur in both free and combined forms .

- (3) That the value for the isotope ratio for sulphur from the original magmatic steam at Wairakei may have differed to some extent from that at White Island, owing to differences in the character of the magma, or the stage reached in volcanic activity.
- (4) The loss of H_2S gas as mentioned above.

If there has been no loss of H_2S gas and the isotopic enrichment ratio for sulphur in the hot chloride water was initially the same as that of magmatic sulphur at White Island ($\delta^{34}\text{S} - 17.5\text{‰}$), then, after the formation of sulphate, the $\delta^{34}\text{S}$ value of the sulphide should be -22.8‰ . If, however, 90% of the original gas has been lost at a temperature of 370°C , the remaining sulphide would have a $\delta^{34}\text{S}$ value of -18.2‰ . This is considerably nearer the actual value -15.6‰ than 22.8‰ , the expected value for no loss.

There are other grounds supporting the conclusion that a considerable amount of gas has been lost from the chloride water. The gas content of the whole discharge is low, about 0.02 mole per 100 mole of water. The gas content of magmatic steam is about 3% by volume, so that if no gas had been lost the gas content of the discharge should be between 1 mole and 0.3 mole per 100 mole of water, for a content of magmatic steam between 30% and 10%. The carbon dioxide content of the discharge in relation to chloride is also low, the molecular ratio of carbon dioxide to chloride being about 1:10, whereas in volcanic exhalations the ratio is more nearly 1:1. Further evidence is also available from the amount of ammonia in the bore discharge. It is likely that ammonia has been formed by the combination of nitrogen (brought in like oxygen in solution in the ground water) with hydrogen in the magmatic steam. The amount of nitrogen that could be in solution in the ground water is much more than would account for the ammonia, as well as the nitrogen, still present in the gas. The argon content of this nitrogen in the steam of the bore discharge is about 3 to 4%. If gas had not been lost from the underground chloride water, the argon content should be much higher than this. Apparently ammonia is formed by the combination of some of the nitrogen in the ground water with hydrogen, the amount being determined mainly by the hydrogen available; and then much of the nitrogen and argon left is lost with the other gases. As ammonia is very soluble, it is not so readily lost.

It has already been pointed out by Ellis and Wilson (1955) that certain of the characteristics of the bore discharges indicate that beneath most of the Wairakei area there is a fairly uniform body of hot water. This is substantiated by the nearly constant gas content, by the chloride content, and by the constant ratios of chloride to boric acid, to fluoride, and to arsenic. If this water had originally a much higher gas content, the question arises as to how this gas was lost.

It may be that a reservoir of hot water has been in existence for a long time, gradually losing steam and gas. Another possibility is that a deep reservoir is gradually losing gas through escape of gas and steam at the upper surface of the hot water, and this cannot be quickly enough replaced by gas working its way up from beneath, so that a concentration and temperature gradient is established. In this case, the time that has to be postulated for the existence of the reservoir is only that necessary for the gradient of gas concentration to be set up. However, there is no evidence that the gas content of the chloride water becomes greater with depth. It may be that only water near the upper surface of the hot water has so far been tapped, and there has not yet been time for the withdrawal of water from the bores to have the effect of bringing up water of appreciably deeper origin. Nevertheless, it seems hard to conceive a very large reservoir of water under the limited active area at Wairakei, as it must be so deep that it would reach into depths where the porosity of the strata is very low. It seems more feasible to suppose that the mixing of ground water with magmatic steam does not occur under Wairakei but elsewhere, nearer to Lake Taupo, and that the flow has been horizontally through porous or fissured beds, and that the loss of gas has occurred on the way. Some indication of where the loss has taken place would be the active areas between Wairakei and Lake Taupo. Such a slowly moving body of hot water in porous or fissured country of at least a few miles in length and of unknown lateral extent would provide the reservoir of water of uniform composition that is called for by the chemical investigations.

CONCLUSION

The $\delta^{34}\text{S}/^{32}\text{S}$ sulphur isotopic enrichment ratio ($\delta^{34}\text{S}$) with respect to sea-water sulphate has been measured for sulphide and sulphate in eleven geothermal bores. The sulphide is depleted in $\delta^{34}\text{S}$ with respect to sulphate by 1.7%.

If sulphur isotopic equilibrium exists in the hot chloride water underlying Wairakei, from partition function calculations it can be shown that the equilibrium temperature corresponding to the $\delta^{34}\text{S}$ values for sulphide and sulphate measured, would be $370 \pm 70^\circ\text{C}$.

The average $\delta^{34}\text{S}$ value for the bore discharges -9.6‰ , is higher than what would be expected if the sulphur was entirely of magmatic origin, as measured for White Island fumaroles where the average $\delta^{34}\text{S}$ value is -17.5‰ . This difference could be partly explained by the loss of hydrogen sulphide from the hot chloride water after the formation of the sulphate, or to a difference in character of the magma underlying Wairakei. Chemical evidence, such as the low gas content of bore discharge and the percentage of ammonia and argon in the discharges, suggests that there has been a considerable gas loss.

Sulphur isotopic evidence put forward in this paper supports additional geochemical evidence that beneath Wairakei there is a

fairly uniform body of hot water and that mixing of ground water with magmatic steam does not occur under Wairakei but nearer to Lake Taupo.

ACKNOWLEDGEMENTS

The writers wish to express their appreciation to Mr W. J. McCabe and Mr G. Patchett for assistance in collection of the samples; to Miss J. B. Ferry for assistance in the chemical preparation of samples for the mass spectrometer; to Mr J. R. Hulston for assistance with the mass spectrometer measurements; and to Dr W. H. Melhuish for partition function calculations.

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RAPID MEASUREMENT OF THE FIBRE DIAMETER OF ROMNEY CROSSBRED WOOL BY THE AIRFLOW APPARATUS

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(Received for publication, 29 October 1957)

Summary

The standard error of estimate of the fibre diameters of 115 wool samples tested on the Wool Industries Research Association (W.I.R.A.) airflow apparatus as compared with the projection microscope mean diameters was 0.92μ .

Data are presented showing the effect on the airflow determination of changes in humidity, regain, medullation, and sample weight.

Measurements on repeatability and variations in fibre diameter within staples have also been made.

INTRODUCTION

With the increasing awareness of the necessity for better quantitative methods of fleece measurement, a simple method is required for the measurement of fibre diameter. Measurement of fibre diameter by means of the projection microscope is so tedious and time-consuming as to be impractical in most circumstances for large-scale experimental work.

Over the past few years simple and rapid techniques which give a measure of mean fibre diameter have been evolved, depending upon the fact that when an air current is passed through a mass of fibres the ratio of airflow to pressure is determined by the total surface area of the fibres, if the arrangement of the fibres in the mass is standardised. Two types of apparatus depending on this principle have been developed. They are the American "Micronaire" (Robinson, 1957) in which air is blown through a plug of wool fibres, and the English W.I.R.A. airflow apparatus (Anderson, 1954) in which air is sucked (drawn) through the fibre plug.

Both types of fibre diameter meter are now quite widely used for the rapid determination of the mean fibre diameter of tops. They do not, however, give any measure of the variability of fibre diameter within a sample. While this limitation precludes their use for some research problems, in most investigations only the mean diameters are used even when obtained by the projection microscope technique.

This investigation was aimed at determining the value of the airflow apparatus for measuring the diameter of scoured wool, with particular

reference to fleece samples of Romney Crossbred wool, and to measure the effect of various factors that may affect the airflow determination.

Such investigations as have previously been made into the use of these meters for the determination of the diameter of scoured wool have been largely concerned with fine wools 30μ or less in diameter. The United States Department of Agriculture (1951) scoured 170 samples of greasy wool, then homogenised them on a small carding machine. When the samples were tested on a "Micronaire" apparatus a curvilinear relationship was found between the float height (in inches) and the mean fibre diameter as determined by the projection microscope short-fibre width method. The standard error of the estimate was found to be $\pm 0.82\mu$. As the result of a test with a small number of samples, the W.I.R.A. (1956) does not recommend the airflow apparatus for measuring the diameter of scoured, hand-teased, wool samples. However, the airflow apparatus was standardised against tops and a different packing factor may be involved, which would require a separate float scale for scoured wool. The W.I.R.A. considers that there is a linear relationship between airflow as measured by float height and the mean fibre diameter.

It is estimated that the 190 scoured Merino samples measured on the projection microscope and the Micronaire by Lang and Wright (1956) had a standard error of the Micronaire estimate of approximately 1.0μ . These authors found that careful hand carding before testing was very important, insufficient carding resulting in low Micronaire readings.

MATERIALS AND METHODS

Apparatus

All airflow measurements were made on a W.I.R.A.-type fineness meter similar to version B described by Anderson (1954). The mass of wool tested was 2 g using a cell pressure-drop of 16 cm of water and a variable flow rate of from 5 to 24 litres of air per minute.

Fibre diameter readings were taken from a linear scale beside the flow meter, which had been calibrated directly in microns from some earlier experiments with tops. This linear scale ranged from 17 to 47μ and was subdivided into 0.2μ divisions; one inch represented 2.60μ .

Projection microscope measurements were made on a Reynolds and Branson instrument, a minimum of 500 fibres per sample being measured at 500 magnifications, from which the (length-biased) mean diameter was calculated.

Preparation of Wool Samples

Samples of greasy Crossbred wool weighing from 10 to 15 g were placed in bags made of cotton mosquito netting and scoured in a solution containing 0.2% nonionic detergent and 0.5% sodium bicar-

bonate at 120° to 130°F. The samples were passed through a wringer and rinsed twice with further squeezing. After drying to a low regain the samples were hand teased and conditioned for at least 24 hours at 68°F and 65% R.H. before testing.

The residual grease content of 4 samples from each of 5 tests ranged from 0.06% to 0.47% with a mean of 0.27% while residual suint contents ranged from 0.09% to 0.28% with a mean of 0.18%.

A sample of approximately 5 g was sub-sampled from the bulk sample. This subsample was thoroughly mixed and teased and from it two 2 g samples were weighed to ± 0.001 g. Each of these 2 g samples was tested twice on the airflow apparatus, being re-teased between tests. The remainder of the bulk sample was similarly mixed and teased, sectioned with a modified Hardy microtome and mounted in cedar wood oil for measurement on the projection microscope.

RESULTS

A. The Relationship of Airflow to Projection Microscope Measurements of Fibre Diameter

As the projection microscope is the accepted instrument for the measurement of fibre diameter, the relationship of the airflow measurements to the projection microscope measurements is of fundamental importance.

Four series of samples were tested on the airflow apparatus and the projection microscope, as follows:

- (1) 66 samples of Romney Crossbred wool ranging from 30 to 42μ with a mean of 37.3μ , the mean sample standard deviation calculated from the total variance being 8.55μ with a sample standard error of 0.37μ .
- (2) 21 samples of Romney Crossbred wool with a similar range of diameters to those in (1) but of only 4 months' growth.
- (3) 18 samples of tops ranging from 20 to 38μ with a mean of 28μ .
- (4) 10 samples of Corriedale wool, card sliver, noil, and tops ranging from 23μ to 29μ .

All airflow measurements are the means of 4 tests, 2 on each of 2 sub-samples.

Figure 1 shows the airflow measurements for the 115 samples plotted against the projection microscope diameters.

The regressions of the mean airflow measurement (Y) on the projection microscope mean diameter (X) for groups 1, 2, and 3 and for the combinations of groups are

Group 1					$\hat{Y} = 0.8748 X + 5.890$
Group 2					$\hat{Y} = 0.9628 X + 2.061$
Group 3					$\hat{Y} = 0.9998 X + 1.323$
Group 1 & 2					$\hat{Y} = 0.9019 X + 4.752$
Group 1, 2, 3. & 4					$\hat{Y} = 0.9827 X + 1.678$

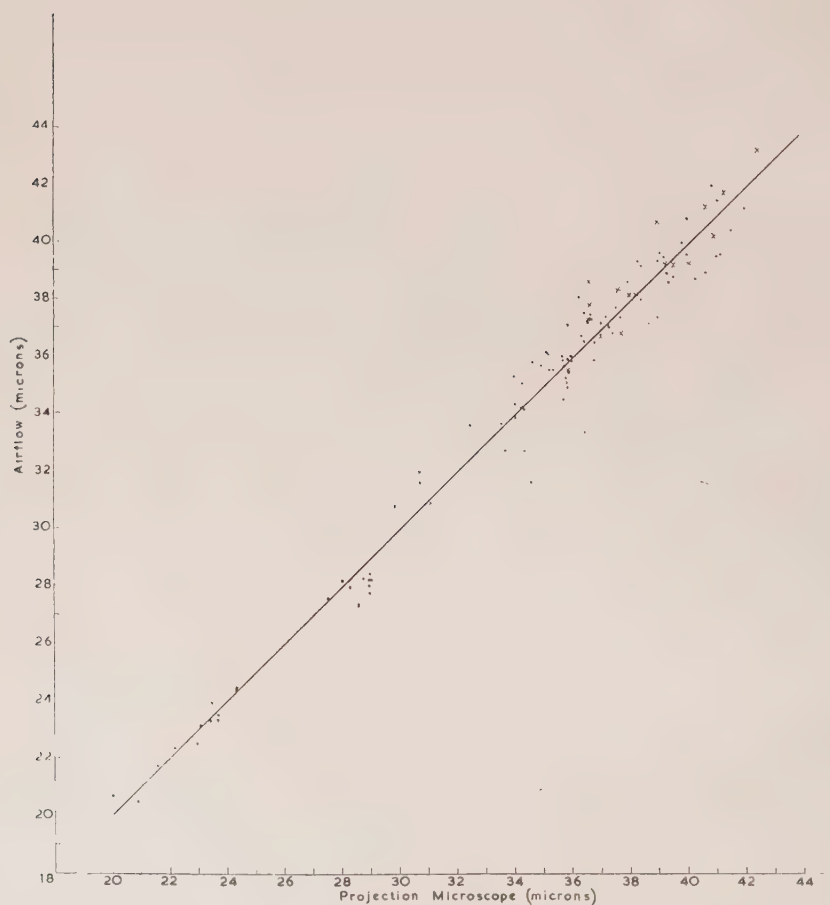


FIG. 1.—Relationship of airflow readings (-1.3μ) to projection microscope readings.

· < 10% medullated fibres

x > 10% medullated fibres

The airflow fibre measurements based on the above regressions for projection microscope diameters of 20, 30, and 40 μ , together with the correlation between the airflow and projection microscope measurements and the standard errors of the regressions are given in Table 1.

TABLE 1.—Relationship of Airflow and Projection Microscope Measurement.

Group	No. of samples	Correlation of AF* and PM† measurements	Std. Error of AF estimate (μ)	AF readings for PM diameters of		
				20 μ	30 μ	40 μ
1	66	0.942	0.769	—	32.1	40.9
2	21	0.923	1.400	—	30.9	40.6
3	18	0.997	0.474	21.3	31.3	41.3
1, 2	87	0.930	0.973	—	31.8	40.8
1, 2, 3, 4	115	0.986	0.917	21.3	31.2	41.0

*AF = Airflow;

†PM = Projection Microscope

It will be seen from Table 1, that there is a very high correlation between the airflow and the projection microscope measurements of fibre diameter, and that the standard errors of the airflow measurements from the regressions are relatively low, so that the airflow apparatus gives a very useful measure of fibre diameter. The best agreement was obtained with group 3, the tops, and the results show that by raising the airflow scale 1.3 μ an exact linear agreement exists for this group between projection microscope and airflow measurements over the whole range of fibre diameter measurements.

The high results found in the airflow apparatus for the tops shows that the scale had been set to read 1.3 μ too high, and that it is not a true difference between scoured wool and tops which resulted in high airflow readings for groups 1 and 2. If there is a different packing factor for randomly packed scoured wool it cannot be greatly different from that for tops.

The standard error of the estimate was considerably lower for the tops than for the scoured samples; these had a standard error of estimate of a similar order to those found by other workers previously cited. Two-thirds of the samples measured on the airflow apparatus will therefore be within 1 μ , and 95% within 2 μ , of the projection microscope mean diameter.

B. Accuracy and Repeatability of Airflow Tests

Working with tops Anderson (1954) found that the variance between samples was less than between repackings, and recommended that 4 tests be made on each of 2 samples of the top.

The U.S.D.A. (1951) found the between-sample variance larger than the between-test variance on small samples of scoured greasy wool which had been homogenised on a small carding machine.

To check the accuracy and repeatability of airflow tests, measurements were made on 206 samples of scoured conditioned Crossbred wool. From the 206 bulk samples which averaged about 10 g, two sub-samples were withdrawn, hand teased and 2.000 ± 0.001 g weighed off. Each sub-sample was tested, re-teased, and re-tested.

Table 2 shows the test and sub-sample means for the 206 samples.

TABLE 2.—Airflow Repeatability Test Results.

	Sub-sample A		Sub-sample B	
	Test A ₁	Test A ₂	Test B ₁	Test B ₂
Test Mean				
Diameter (μ)	37.487	37.670	37.454	37.668
Sub-sample Mean				
Diameter (μ)	37.579		37.561	

The results of an analysis of variance carried out on these airflow tests and the components of variance are given in Table 3.

TABLE 3.—Analysis of Variance of Airflow Tests.

Source of Variation	Degrees of freedom	Mean square	Components of variance
Between tests	411	0.166	$2\sigma_t^2$
Between sub-samples	205	0.719	$8\sigma_s^2 + 4\sigma_t^2$

The components of variance, calculated from the analysis were:

$$\text{Sub-sample } \sigma_s^2 = 0.048.$$

$$\text{Test } \sigma_t^2 = 0.083.$$

The component of variance due to test was thus almost twice that due to sub-sample. Increasing the number of sub-samples to three with only one test per sub-sample will give a similar error variance to two tests on each of two sub-samples.

As weighing out of sub-samples is the most time-consuming part of the airflow test, an increase in the number of sub-samples would tend

to defeat the object of using the airflow apparatus, which is to obtain a rapid estimate of fibre diameter.

It was observed that there were more than twice the number of negative values of Test A_1 minus A_2 or B_1 minus B_2 than there were positive values, resulting in the higher means of Tests A_2 and B_2 . A t -test of 9.95 showed that the mean difference between repeat tests of 0.199μ differed highly significantly from zero, and that a systematic error was involved in the testing.

The most probable explanation of the increase in airflow readings for the second test is that there has been a reduction in the weight of the sample due to the loss of fine fibres and fine dirt during re-tesing, and/or to loss in weight due to the "vacuum cleaning" action of the air current during testing. That loss of fine fibres and dirt does occur during testing is apparent from the fine deposit which visibly collects around the airflow apparatus where the samples are re-tested.

The increase in apparent mean diameter of 0.2μ between the first and second tests of the original series of samples is sufficiently large to warrant a correction for this factor in the interpretation of airflow test data. The second test does give a guide as to whether the first test has been performed correctly and the error variance is lower than if only 1 test is made on each of 2 sub-samples. The correlation between the first tests on the two sub-samples (A_1 and B_1) is very high ($r=0.981$), so that where group comparisons only are desired the testing of single samples should suffice. Where individual results are of more importance, 2 tests should be made on each of 2 sub-samples, making allowance for an increase in the second test.

TABLE 4.—Loss in Weight During Testing.

				No. of samples	No. of tests	Mean loss in weight (mg)	Mean increase in airflow reading (μ)
Scoured	Crossbred			95	2	4.0	0.07
Scoured	Crossbred			18	3	10.5	0.12
Scoured	Crossbred			18	3	9.8	0.18
Tops A				6	{ 2	5.6	0.03
					{ 4	6.2	0.13
Tops B				10	{ 2	3.2	0.03
					{ 4	4.7	0.08

Table 4 shows the mean loss in weight between the initial and the final weight for the three series of Crossbred wools. In the first series the 95 samples were tested twice, and in the second and third series

the samples were tested three times, having been teased before each repeat test. In each series there was an appreciable loss in weight during testing, associated with an increase in airflow reading. The samples tested three times lost more weight than those tested twice.

Six samples of tops (A) were weighed after the sampling procedure recommended by Anderson (1954), teased to obtain a random distribution, then packed into the airflow chamber. The samples were tested four times, being teased before each repeat test. Table 4 shows the mean loss in weight after 2 and 4 tests and the associated increases in airflow reading.

The 10 tops of series (B) were similarly treated with the exception that the samples were thoroughly teased before the initial weighing. As would be expected the series B tops show a slightly smaller loss in weight than the series A tops and also less increase in airflow reading.

While the mean increases in airflow reading of these tops were very small, increases for some individual samples were quite appreciable.

C. Sample Weight and Airflow Readings

To measure the accuracy required in weighing samples for airflow testing, four tests were carried out at three different weights on seven samples. Table 5 shows the results of these tests, the samples in each case being weighed to ± 0.001 g.

TABLE 5.—Effect of Sample Weight on Airflow Readings.

Sample No.	Airflow Reading (μ) at different weights			Airflow Difference (μ) 1.900 g-2.100 g
	1.900 g	2.000 g	2.100 g	
332	45.3	42.0	38.8	6.5
365	43.5	40.1	36.3	7.2
336	42.8	40.0	36.9	5.9
522	39.4	36.5	33.6	5.8
340	37.6	35.2	32.6	5.0
435	35.7	33.0	30.2	5.5
386	34.7	32.4	29.8	4.9
Means	39.9	37.0	34.0	5.8

With increasing sample weight there is a marked reduction in airflow reading, owing to the greater surface area of the fibres retarding the passage of the air. As would be expected this effect increases with increasing diameter and is therefore more important in terms of microns when measuring Crossbred as compared with Merino wool.

As a weighing error of only 10 mg is approximately equivalent to an airflow difference of 0.3μ , careful weighing must be carried out if large individual errors are to be avoided. The change in airflow measurements associated with a given change in weight of these samples is larger than that shown in Table 4 for the increase in airflow readings during re-testing of samples, and it is also higher than that found by Richards (1954).

D. Relative Humidity, Regain, and Airflow Measurements

As fibre diameter varies depending upon regain, and so upon the relative humidity of the air in which samples are conditioned, airflow determinations should be made where possible under standardized atmospheric conditions. The regain of the wool in a standard atmosphere will also depend upon whether the samples have been conditioned from a wet or a dry state, which may cause regain differences of up to 2%. Where possible it is preferable to dry samples to a fairly low regain before conditioning and testing in a standard atmosphere (*c.f.* B.S. 1051, 1953). At a low R.H., the fibre diameter will be smaller but more fibres will be needed to make up the 2 g sample. Anderson (1955) has published figures for correcting the results of tests made at various relative humidities to 65% R.H. These corrections are based on the increase in radial swelling of wool fibres with increasing regain, and their accuracy depends on a constant relationship of regain and R.H. Unless temperature variations are very large they may be ignored as they have only a small effect on the moisture content of the wool at constant R.H. Temperatures ranging from 50° to 80° F had no apparent effect on the airflow readings given by two perforated duralumin plates which gave air flows equivalent to fibre diameters of approximately 20 and 40μ .

Tests were carried out to determine the relationship of relative humidity, regain, and airflow readings for Crossbred wools. In all, five groups of wools were tested at different relative humidities. The general procedure for groups 1 to 3 was to oven-dry the samples and then test them at increasing relative humidities, the temperature being 68° F. Two grams were tested at each humidity and the whole sample was weighed so that the regains at each of the humidities could be calculated, knowing the oven-dry weights. In groups 4 and 5 the samples were oven-dried after testing at increasing R.H. Groups 1 to 3 covered the normal range of Crossbred diameters, while the diameter range in groups 4 and 5 was approximately 2μ in each group.

The results of these tests given in Table 6 show that airflow reading increases with increasing R.H. These averages conceal the fact that some samples in tests 1 to 3 reacted rather erratically to increasing R.H. There were also quite marked differences in regains at similar R.H. The differences in reading at different R.H. are sufficiently large to necessitate correction factors for comparison of tests carried out at different R.H. There is, however, no definite regain for a given R.H.

TABLE 6.—Effect of Relative Humidity on Diameter.

Group	Number of samples	Relative humidity (%)	Mean regain (%)	Radial swelling (%)	Mean fibre diameter*		
					A	B	C
1.	13	51	13.4	5.7	37.7	37.2	37.7
		65	16.4	7.2	37.9	37.9	37.9
		75	17.2	7.6	38.0	38.1	37.6
2.	13	55	12.9	5.5	37.9	37.6	38.0
		65	14.8	6.4	38.0	38.0	38.0
		74	16.3	7.1	38.1	37.9	37.7
3.	12	56	14.6	6.3	38.3	38.6	38.6
		65	16.3	7.1	38.5	38.5	38.5
		78	17.2	7.6	38.7	38.5	38.0
4.	5	52	10.6	4.3	30.5	31.1	30.9
		65	14.8	6.4	31.3	31.3	31.3
		75	17.1	7.5	31.6	31.3	31.2
5.	5	52	10.6	4.3	40.0	40.8	40.5
		65	14.8	6.4	41.1	41.1	41.1
		75	17.1	7.5	41.5	41.1	41.0

*A from airflow measurement.

B corrected to 65% R.H. from radial swelling data.

C corrected to 65% R.H. according to Anderson (1955).

150 samples of Crossbred wool in 20 tests carried out over a period of a year were found to have a mean regain of 15.05% with a standard deviation of 0.90% when conditioned for at least 24 hours at 68°F and 65% R.H. after drying to a low regain.

Over the range of regains from 8 to 20 the percentage radial swelling increases approximately linearly from 3.0 to 9.0 (Warburton, 1947), so that a change of 1% in regain is associated with a change of 0.5% in radial swelling.

In Table 6 the percentage radial swelling at each regain is given and from these figures the mean fibre diameters at 65% R.H., based on the radial swelling at 65% R.H., are calculated for each group of tests. The mean fibre diameters based on the corrections given by Anderson (1955) are also shown. The results based on Anderson's correction factors are not as satisfactory as those based upon the individual regains, because of the different regains associated with the same R.H. Where a standard atmosphere is not available but there are facilities for determining regains, the use of correction factors based on regain and not on R.H. would appear to be more satisfactory. Table 7 gives factors for correcting fibre diameters at regains from 10 to 20% to a standard regain of 16%.

TABLE 7.—Regain Correction Factors.

Regain (%)	Correction factor
10.0	1.030
12.0	1.020
14.0	1.010
16.0	1.000
18.0	0.990
20.0	0.980

Another method of correcting for differences in R.H. is by testing a sample of top of known fibre diameter at the same time as the trial samples. Care must be taken to see that the top has had the same treatment before airflow testing as the trial samples.

E. Medullation and Airflow Measurements

Since medullated fibres have a larger surface area in relation to their weight than normal fibres, medullated wool samples would be expected to give low diameter readings when measured on the airflow apparatus. Richards (1954) has calculated the decrease in the airflow diameter associated with decreasing density of the wool sample.

Only a small percentage of Crossbred wool is completely free from medullation, the incidence of which increases with increasing fibre diameter. The percentage of medullated fibres was determined in the 66 samples of group 1 used in relating airflow to projection microscope diameter measurements. Twenty-seven of these samples had more than 5% medullated fibres and 10 had more than 10%. Omitting the samples with more than 10% medullated fibres from the airflow regression (Y) on the projection microscope diameter (X), the following regression for the remaining 56 samples was obtained.

$$\hat{Y} = 0.8621 X + 6.341, \text{ with a std. error of } \pm 0.767\mu.$$

Diameters calculated from this regression are almost identical with those from the regression based on all the samples, showing that in this group medullation had no measureable effect on airflow reading. This is also apparent from Fig. 1 in which the samples with 10% medullated fibres are indicated by an X, while those with less than 10% medullated fibres are indicated by dots. For the 27 samples with more than 5% medullated fibres there was no significant correlation between the percentage of medullated fibres and the deviation from the regression; $r = -0.112$.

Degree of Medullation.—Seventeen Crossbred samples were chosen, 6 from group 1, and 11 from group 2, to cover the whole range from

0 to 43% of medullated fibres. The samples were benzol tested (Belin, 1949) and the percentage by weight of medulla was also measured (Ross and Speakman, 1957). Even the sample containing 43% of medullated fibres contained only 1.30% by weight of medulla calculated on its conditioned weight, the next highest being 0.78%, while the group mean was only 0.36%. There were significant correlations between the percentage of medullated fibres with the benzol test, and also with the percentage of medulla by weight, of 0.928 and 0.505 respectively.

While more data on this topic is desirable it would appear that unless the sample is heavily medullated the airflow reading will not be greatly affected.

F. Effect of Fibre Diameter Distribution on Airflow Reading

As the airflow reading is a function of the total surface area of the sample, wools with the same mean diameter but different diameter distributions would have different surface areas for the same weight, and, therefore, different airflow diameters. Mixtures of varying proportions by weight were made between any two of three tops of airflow diameters 23.2, 27.3, and 36.8 μ . Nine such mixtures all had airflow diameters which were lower than the calculated diameters based on the proportions by weight of the tops in the mixture. The differences ranged from 0.23 μ for a 1:3 or 3:1 mixture of the 23.2 and 27.3 tops to 1.55 μ for a 1:1 mixture of the 23.2 and 36.8 μ tops, with a mean difference of 0.76 μ . Calculated on surface area, however, the difference from the measured diameters ranged from -0.42 μ to +0.30 μ with a mean difference of only 0.17 μ .

Such diameter distributions are unlikely to be met with in normal practice, unless perhaps when dealing with "primitive" wools. Medulation of such wools would no doubt preclude the use of the airflow apparatus for measuring their diameters.

In the top mixtures the length-biased projection microscope mean diameter would be more affected by the finer fibres than the airflow measurement resulting in a low projection microscope mean diameter for a sample with such a fibre distribution.

G. Within-Staple Variation in Fibre Diameter

Two series of results from other experiments show the value of the airflow apparatus for determining the variations in fibre diameter which occur along a staple.

In the first series, two groups of a hundred sheep were sampled at 4-monthly intervals. The 3 mean 4-monthly and the 12 months' fibre diameters are given in Table 8 together with 12 months' fibre diameters calculated from the 4-monthly diameter figures, making allowances for the different weights of the samples.

TABLE 8.—Variations in Fibre Diameter Within Staples.

Period of growth	First Series		Second Series	
	Group 1 Diameter means (μ)	Group 2 Diameter means (μ)	Bisected staples (Mar.-Jul. samples)	Mean diameter (μ)
Nov.-Mar.	36.48	36.11	Staple tips	36.32
Mar.-Jul.	35.03	34.32	Staple butts	33.60
Jul.-Nov.	32.07	32.07		
12 months calculated (weight- corrected)	35.18	34.74	Full staple calculated (wt.-corrected)	34.87
12 months actual	34.75	34.35	Full staple before cutting	34.68

In the second series, the March-July samples of the first series were grouped in lots of 10 and cut into "tips" and "butts". The mean diameters for the tips and butts of the 20 groups, together with their weight-corrected mean and the mean of the uncut staples for this group are also given in Table 8.

In groups 1 and 2 the weight-corrected mean totals of the 3 4-monthly samples are 0.43 and 0.39μ respectively higher than the means of the 12 months' samples. Similarly, while all the butts were finer than their respective tips, with a mean difference of 2.72μ , the weight-corrected mean diameter is 0.19μ higher than the mean diameter before the staples were cut.

As there are differences in diameter, both between the 3 4-monthly samples and along the individual samples, there will be differences in fibre diameter distribution. The full year's samples and the uncut March-July samples are analogous to the mixtures of tops (section F) which, on a weight basis, have a lower airflow diameter than the mean of the two tops of which they are composed. On this basis one would expect the weight-corrected mean diameter of the tips and the butts to be higher than the mean diameter before the staples were cut, as is actually found.

Anderson (1949) found that packing and the length of fibres affected the rate of airflow. However, in the tests on cut staples, while the fibre lengths are different, no consistent error would be expected from packing as all samples were thoroughly hand teased before testing.

To check the effect of fibre length on airflow, five samples of tops were cut up into lengths from $\frac{1}{4}$ in. to $1\frac{1}{2}$ in., and samples of each length were airflow tested. Only 2 of the 5 tops showed any indication of an increase in airflow reading with decreasing lengths, the other three tops giving consistent readings irrespective of length. A more

detailed study of this point is required, however, before the presence of any length effect can be eliminated.

DISCUSSION

The preceding results show that the airflow apparatus gives a very satisfactory measure of the diameter of scoured samples of Romney Crossbred wool. The standard error of the airflow estimate relative to the projection microscope measurements of about 1.0μ is reasonably low, so that group comparisons based on small numbers of samples may be made.

A similar degree of accuracy would be expected for Crossbred samples tested on the Micronaire. The airflow apparatus, because of its simplicity of construction and method of use, and the fact that it draws conditioned air from the room through the samples, is probably less liable to errors than the Micronaire in which the air must first be compressed, thus altering its temperature and relative humidity. Perforated metal "masters" were made which allowed air to pass through the airflow apparatus at rates corresponding to fine and coarse fibre diameters. The airflow apparatus was checked against the "masters" at irregular intervals over a period of a year, but it was never found necessary to alter the position of the float scale.

Variations in the design of the airflow apparatus to test larger samples where less accuracy in weighing would suffice, or for very small samples of wool should be easy to construct. The principle of this method has been used by Settle (1955) to measure variations in diameter along single wool fibres.

The projection microscope mean fibre diameter of cross-sections taken at different levels in a single Crossbred staple has been found in this laboratory to vary over a range of about 10μ . The marked seasonal changes in diameter (Story *et al.*, 1956) frequently make the interpretation of diameter measurements made at one particular level in the staple, very difficult. The effect of differing treatments on wool growth is usually spread over a period of months rather than days. For this reason the airflow technique may in many cases give a more accurate measure of the treatment effect than the use of a single staple cross-section technique.

The use of the airflow apparatus should enable work on the characterisation of the fleece of the New Zealand Romney Crossbred to be more fully investigated. It is possible that factors which affect the airflow measurement of fibre diameter are relatively constant for individual sheep.

The scouring of greasy wool samples is satisfactorily accomplished in a domestic washing machine. Care must be taken, however, to avoid felting the wool. Long wool samples scour satisfactorily in bags of cotton mosquito netting, while samples of very short staple length need to be scoured in bags of fine cotton cloth to avoid fibre loss.

It is important to wring out the bags thoroughly after scouring and rinsing as a large proportion of the grease and suint is removed during the wringing.

The preparation of the samples before weighing and testing can be satisfactorily speeded up by the use of hand cards. In this connection the development of a card or gilling machine for handling small wool samples without appreciable fibre loss would greatly increase the rapidity of the airflow fibre diameter determination. The screwing and unscrewing of the cap on the wool chamber can be both simplified and speeded up by the use of a plunger. The plunger fits through the screw cap on to the upper lip of the inner wool chamber, while a narrower portion continues a short distance down inside the inner wool chamber. Pressure is applied to a handle on the plunger when screwing or unscrewing the cup so that the wool does not force the inner wool chamber against the cap, thus making it difficult to turn. A hole is bored through the plunger to avoid disturbing the liquid in the manometer when the plunger is inserted. The plunger is never left in the chamber during testing.

It is unlikely that the amount of medulla present in what are graded by eye as non-hairy Crossbred samples is sufficient to affect the airflow estimate materially. However, further work is required before it is possible to assess at what level allowance must be made for medullation in the interpretation of airflow data.

ACKNOWLEDGEMENTS

The author is indebted to Dr R. M. Williams, Director of the Applied Mathematics Laboratory, Department of Scientific and Industrial Research, for guidance with the statistical analysis involved in this paper and to Dr L. F. Story, Director, New Zealand Wool Industries Research Institute, for helpful advice and criticism.

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